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NIKOLAI IGNATYEVICH NIKITIN

(A Scientific and Biographical Sketch on his Sixtieth Birthday and the Thirty-Sixth Anniversary of his Scientific and Teaching Career)

Nikolai Ignatyevich Nikitin was born in 1890 in St. Petersburg, the son of an office worker. He completed high school in 1907 and entered the St. Petersburg Institute of Forestry (now the S.M.Kirov Academy of Forestry), from which he graduated in 1913 with honors.

While still a student Nikolai Ignatyevich began to work in the analytical chemistry laboratory. Over and above the prescribed experiments, he worked through the practical manual of organic chemistry, after which he commenced a minor bit of research under the guidance of his instructor, V.N.Krestinsky (subsequently professor of organic chemistry at the Academy of Forestry). This research dealt with the decomposition products of allyl alcohol when its vapors were passed over incandescent alumina. The research was successful; it was read at a meeting of the Division of Chemistry of the Russian Physico-Chemical Society and later published. Nikolai Ignatyevich also did work in physical chemistry in the laboratory of Prof. E.V.Biron, under whose guidance he investigated "The Heat of Combustion of Charcoals." This research was published, and it is still in use at the present day. In 1916 the Russian Chemical Society awarded N.I.Nikitin the Prof. M.G.Kucherov Prize for this paper.

As part of his preparatory work for his thesis, Nikolai Ignatyevich spent a summer in the Caucasus, at Borzhom, at the suggestion of N.A.Fillipov, professor of forest technology. There he investigated the filtration of the waters of the Borzhom spring, using charcoal filtration. His goal was the elimination of the disagreeable odor of iodoform from the Borzhom water. This required a study of the carbonization of various species of wood. The problem was successfully solved. The administration of the Borzhom mineral waters awarded a bonus to the student N.I.Nikitin. This research subsequently served as the subject of Nikolai Ignatyevich's thesis. Thus, by the time he had completed the course at the Institute of Forestry, Nikolai Ignatyevich had already earned his spurs as a research worker and already had had experience in experimental work.

The outstanding ability of N.I.Nikitin could not fail of notice in the Institute of Forestry, and he was appointed an assistant to the chair of wood technology in January, 1914, though a year later he shifted to the post of assistant to the chair of chemistry. While an assistant to the wood-technology professorship, Nikolai Ignatyevich made a study of the production of cellulose in the Finnish factories, working two months in the cellulose plant in Kotka, where he made his first contact with industry. At that time the Kotka plant was one of the largest cellulose producers in Europe.

During the next seven years Nikolai Ignatyevich worked as an assistant, in charge of analyses for the chair of general chemistry in the Institute of Forrestry. In 1921, after delivering a trial lecture on "The Osmotic Pressure of Solu-

utions," he was appointed an instructor in the Institute of Forestry. During this period Nikolai Ignatyevich carried out several researches in physical chemistry, as well as in the chemistry of wood pulp.

In 1923 he was sent to Germany to study its wood-pulp chemical industry. While there he worked during the winter semester in the physical chemistry laboratory of the University of Goettingen. Nikolai Ignatyevich did his research on "The Pyrophoric Properties of Metals" in this laboratory. The young instructor continued to work in physical chemistry after his return home from Germany (down to 1925). He completed and published research papers on the solution of gases and vapors of volatile liquids by finely divided metals and gels. In these papers N.I.Nikitin demonstrated that he had fully mastered and inherited the brilliant experimental methods of his teachers, Krestinsky and Biron, their rigorously critical approach to the basic premises of a research project and to the evaluation of its results, and their vivid and concise presentation.

In 1925 N.I.Nikitin began his scientific activity in what was then a wholly new field - the chemistry of wood pulp and cellulose. He was commissioned to organize a chair of the chemistry of wood pulp and cellulose in the Institute of Forestry and was appointed to that professorship.

This turn in the scientific career of Nikolai Ignatyevich was far from accidental. Research on the high-polymer constituents of wood pulp, which engaged the attention of many scientists at that time, was feasible only with a fundamental knowledge of colloid and physical chemistry, in addition to organic chemistry. All the previous activity of N.I.Nikitin had prepared him for this.

Nikolai Ignatyevich set to work in this new field with extraordinary energy. He established the first chair and laboratory of the chemistry of wood pulp and cellulose in the Soviet Union, in which an extensive research program was carried out. He wrote the following monographs: The Chemical Technology of Wood Pulp (1923); Outlines of Wood-Pulp Chemistry (1926); and Colloidal Solutions and Cellulose Esters (1929). The second edition of the last book appeared in 1933 and was awarded a prize by the Committee for the Chemical Development of the USSR.

N.I.Nikitin, with his pupils (N.Y.Solechnik and F.P.Komarov), wrote the textbook The Chemical Technology of Wood (1931), and the monograph Wood-Pulp Chemistry (1935); he wrote the basic textbook The Wood-Pulp Chemical Industry (1938) in collaboration with a group of research workers in the Academy of Forest Technology.

Nikolai Ignatyevich opened wide the doors of the new professorship to the student body. Work went on in the laboratory from morning to night. The well-known professors V.I.Sharkov, D.Sc., and N.Y.Solechnik, D.Sc., and a number of instructors and candidates of science: V.I.Yuryev, T.I.Rudneva, I.M.Orlova, N.V. Lebedev, F.I.Korchemkin, I.A.Solovyev, and others, have come from the students who worked in N.I.Nikitin's laboratory. Moreover, many other research workers were trained in N.I.Nikitin's laboratory.

N.I.Nikitin established close links with industry from the very first days of organization of the chair of the chemistry of wood pulp and cellulose. Research projects were carried out in the laboratory for the account of industrial organizations and factories. During the period 1925-1930, N.I.Nikitin's chair was one of the most active in the Institute of Forestry; in particular, work was done on the synthesis and the properties of cellulose for what was then a new branch of industry - the production of artificial silk. These research projects

were among the first to be done in the Soviet Union, and they exerted considerable influence upon the development of this branch of industry.

From the very founding of the chair of wood-pulp and cellulose chemistry, N.I. Nikitin devoted a large amount of time to teaching the new subject. He is a brilliant lecturer, who has been and is extremely popular with the student body. Nikolai Ignatyevich took an active part in the establishment of the Faculty of Chemical Technology in the Forestry Institute, as chairman of the committee on the chemistry curriculum, deputy dean of the faculty, etc. In 1929 N.I.Nikitin was promoted to the rank of full professor.

The research done by N.I.Nikitin and his co-workers (from 1925 to the outbreak of World War II, i.e., to 1941) dealt with the synthesis and the properties of cellulose esters: benzyl and ethyl cellulose, butyl cellulose, amyl cellulose, cellulose, and the phthalic esters of cellulose, as well as with the chemical composition of wood pulp and hemicellulose (especially arabogalactan from Siberian deciduous trees) and the synthesis of cellulose for synthetic fiber.

In connection with the latter, N.I.Nikitin was one of the first in the Soviet Union to work out a technical method for determining the viscosity of cellulose, which has been of great importance to industry.

N.I.Nikitin likewise did much research in the field of wood-pulp lignin. The most interesting result of his work on lignin was the extraction from wood pulp of a lignin that was close to the natural product (extraction with dioxane under extremely mild conditions), which has been quite important in shedding light upon the nature of lignin. By 1949 the number of researches carried out by N.I.Nikitin (with his co-workers) totaled approximately 80.

N.I.Nikitin has been a member of the scientific councils of a number of research institutes since 1933 (Wood-Pulp Chemistry, the Paper Institute, etc.), as well as a professor of Leningrad State University, a lecturer on wood-pulp chemistry at the Arkhangelsk Institute of Forest Technology, a permanent member of the editorial board of the Journal of Applied Chemistry, vice chairman of the Committee on Cellulose of the Division of Engineering Sciences of the USSR Academy of Sciences, a member of the Commission of Experts on Forest Technology of the Committee on Higher Education, etc.

In 1937 the degree of Doctor of Engineering Sciences was conferred upon N.I. Nikitin without his having to defend a dissertation. In 1939 Nikolai Ignatyevich was elected a corresponding member of the USSR Academy of Sciences in the Division of Chemistry.

By this time the name of N.I.Nikitin was well known as possessing merited authority among Soviet chemists, as well as in many branches of industry.

Nikolai Ignatyevich has been a pioneer in the establishment in the Soviet Union of such branches of chemistry as the chemistry of wood pulp and cellulose, which is now of such great scientific and industrial importance. Many of our industries are in urgent need of the development of these branches of science, inasmuch as they make it possible to deal with the fundamentals of technological processes, to deliver a product with the requisite technical properties, and to set up new types of production.

During the Great Patriotic War, Nikolai Ignatyevich remained in Leningrad until the end of December, 1941. He did not cease his scientific work, however. At the end of December he was evacuated from Leningrad together with a group of

the professorial and teaching staff of the Academy of Forest Technology.

After a brief stay in the city of Yaransk, Kirov Region, Nikolai Ignatyevich reached Sverdlovsk, where he was assigned to the Urals Institute of Forest Technology and resumed his scientific and teaching activities. At the same time he worked in the Urals branch of the USSR Academy of Sciences, where he did extremely interesting research on lignin.

In 1944, Nikitin returned to Leningrad, where he experienced in full the consequences of the war unleashed by the Fascist German invaders, who brought so much suffering to the Soviet Union and to Leningrad in particular. Though the laboratories of the chair of wood-pulp and cellulose chemistry had not been destroyed, they required fundamental restoration and re-outfitting. All the research work had been disorganized, and - worst of all - Nikolai Ignatyevich no longer had his group of scientific co-workers about him. During the war some of his associates had shifted to other fields, while others had died during the blockade of Leningrad. Only one was left: an instructor, T.I.Rudneva, who had stayed in Leningrad throughout the war. She aided Prof. Nikitin in re-establishing the professorship; the blockade had ruined her health, however, and she did not long survive the end of the war.

During this difficult period Nikolai Ignatyevich again displayed his unbounded energy. His laboratories were re-established and fitted out with the necessary equipment and materials; and he selected a new group of co-workers and re-organized the chair's research work and the training of assistants. This research work was aided by the Forestry Institute of the Academy of Sciences, as well as by industrial and scientific organizations. As a result, N.I.Nikitin's chair was as actively engaged in scientific work as before the war, and the fruits of this work are already at hand.

A thorough study was made, for instance, of the changes in the chemical composition of oakwood pulp as affected by the species of tree, and in that connection a method was developed for the mild aqueous hydrolysis of this wood pulp that was very promising. A study was made of the chemical constitution of the wood pulp coming from the Daursk deciduous forests, and a rational method for its hydrolysis was worked out. In this research considerable attention had to be devoted to the development of precise methods for the identification of sugars. All of this research was carried out in the laboratory of the Institute of Forestry of the USSR Academy of Sciences.

As part of the preparation of candidate dissertations, rather extensive research was done (together with M.A.Mikhailova and S.D.Antonovsky) on the reaction of lignin with acetylene under pressure. This research resulted in the synthesis of vinyl ethers of lignin - readily soluble in ether and in other solvents of synthetic resins.

Prof. Nikitin devoted special attention to a study of the physical and chemical properties of partially esterified and mercerized fibers. Such fiber properties as hygroscopicity, solubility, film formation, and the effect of chilling mercerized fabrics in caustic soda upon the molecular weight were the subjects of this investigation. The low-substituted cellulose xanthogenates, synthesized for the first time and soluble upon chilling, were identified in very great detail. This research is of considerable interest to industry, which is making more and more use of low temperatures to facilitate the solubility of cellulose in dilute caustic soda (freezing cellulose is a means of increasing the internal surface of the fibers).

The foregoing does not exhaust the researches carried out under the supervision of Prof. Nikitin during the postwar period (1945-1949). Nikolai Ignatyevich's new associates: A.F.Zaicheva, M.M.Chochieva, N.P.Tsvetayeva, N.I.Klenkova, E.A.Abramova, M.K.Mukovnikova, S.D.Antonovsky, and others, participated in all these research projects, in addition to his old co-worker, Instructor T.I.Rubneva (until 1949). Liaison with industry was maintained during these years by his associates F.P. Komarov, instructor, N.G.Yantovskaya, and M.S.Astakhova.

The activities of N.I.Nikitin after the war were not limited to scientific research and teaching. The Presidium of the USSR Academy of Sciences appointed him president of the Leningrad branch of the Commission on the History of Chemistry, and he became acting editor of the Journal of Applied Chemistry. He also had occasion to serve temporarily as acting vice director of the Institute of High Molecular Weight Compounds of the USSR Academy of Sciences, of whose Scientific Council he is a permanent member.

Mention must be made of the extensive lecturing done by Nikolai Ignatyevich at scientific conferences and meetings of scientific councils and learned societies, as well as in industrial enterprises themselves, his appearances as opponent in the defense of doctoral and candidate dissertations, his work in the preparation of fellows, and the like.

There is no room in this brief biographical sketch to describe all of Nikolai Ignatyevich's useful and manysided activites. His scientific work has repeatedly been mentioned in orders of the Academy of Forest Technology and of the People's Commisariat for the Timber Industry. In 1940 Prof. Nikitin was awarded the badge of "Honored Worker of the Timber Industry" by the USSR People's Commisar of the Timber Industry. In 1945, he was awarded the Order of the Red Banner of Labor for his outstanding achievements in wood-pulp chemistry, and in 1946 he was awarded the medal "For Valiant Work During the Great Patriotic War."

For his sixtieth birthday Nikolai Ignatyevich has prepared for the press a new monograph, The Chemistry of Wood Pulp, in the preparation of which the entire staff of his chair had been engaged.

All through his life Nikolai Ignatyevich has not been a man locked up within his own specialty. He has manifested a lively interest in the development of our socialist industry, its requirements and achievements. He has endeavored to relate his research work to the needs of industry. His numerous researches on new derivatives of cellulose (cellulose esters) were carried out in close contact with the newborn industries dealing with the chemical treatment of cellulose, which were required to provide the Soviet Union with the needed new products (plastics, films, lacquers, etc.). Nikolai Ignatyevich's work in this field was of great importance. No less timely were his researches on the physical and chemical properties of cellulose and his development of methods for producing celluloses with the requisite properties. His researches on lignin, on the chemical composition of wood pulp, etc., were undertaken in an effort to discover a way of using wood pulp and its constituents rationally and to shed light upon the essentials of the technological processes involved.

The monographs written by N.I.Nikitin are of value in the practical field, in addition to the their scientific and theoretical significance. They are used by the engineering and technical personnel of many industries, who find them sources of great value in their work.

Nikolai Ignatyevich is actively interested in social life, taking part in

community activities (as a member of the Trade Union Committee of the Forest Technology Academy, as a worker in his election district, and the like) and in the realization of community projects, etc.

The many associates and pupils of Nikolai Ignatyevich know him as an exacting scientific administrator possessing a large fund of erudition. At the same time they look upon him as an elder comrade, a sympathetic and modest man, and they remember their work with him with a feeling of gratefulness.

The foundations of Soviet research and of the Soviet scientific school in the field of wood-pulp and cellulose chemistry, laid by Nikolai Ignatyevich, have been widely expanded by our Socialist government.

Among the large staff of Soviet scientists working in the chemistry of wood pulp and cellulose Nikolai Ignatyevich Nikitin occupies a prominent place.

F.P.Komarov and S.D.Antonovsky

NEW TYPES OF TERPENE TRANSFORMATION. I

D. Tishchenko

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I

The chemistry of the terpenes has, on the whole, developed along the following lines: 1) qualitative and quantitative research on the ethereal oils and turpentines; 2) establishing the structure of their constituents; and 3) studying the transformations of terpenes.

The overwhelming majority of all researches in the third group deal with methods for converting terpenes into substances that are more highly saturated and whose carbon skeletons have been changed (camphor and terpin hydrate, say, from pinene, etc.). As a rule, catalytic and thermal isomerization are not accompanied by an increase in saturation, but effect a profound rearrangement of the carbon skeletons of the terpenes (for example, camphene, α-terpinene, terpinolene, and dipentene from α-pinene; myrcene from β-pinene, etc.). Hence, it is not a matter of chance that the derivatives of even the most accessible terpenes (α- and β-terpenes, carene, and dipentene), which have the same carbon skeleton and the same degree of saturation as the initial terpene, have been investigated only superficially, with far from all of them accessible and known. A small quantity of myrtenol, a primary alcohol corresponding to α-pinene, for example, has been recovered by a complicated method from the ethereal oil of myrtle [1], while no methods of synthesizing it are known; verbenol, a secondary alcohol of the α-pinene series, has been found mixed with the respective ketone in olibanum oil [2]; a secondary alcohol of the β-pinene series has been isolated by a complicated method from eucalyptus oil [3]; and small quantities of carveol, a secondary alcohol of the dipentene series, have been found in oil of caraway [4]; in general no oxygen derivatives of the carenes, the terpinenes, the phellandrenes, the fenchenes, terpinolene, or camphene are known.

It has been known for a comparatively long time that the autoxidation products of the terpenes include alcohols and ketones with the same carbon skeleton and the same degree of unsaturation as the original terpene. In this way, verbenol [5] has been recovered from α-pinene, pinocarveol from β-pinene [6], and carveol from dipentene [7], but this method produces low yields of the alcohols, and recovering the latter is difficult and laborious [8]. Hence, this method is useless for practical purposes.

Papers have recently been published that indicate it is possible to synthesize oxygen-containing derivatives of the terpenes, with unchanged structure and unsaturation, by oxidizing the latter with selenium anhydride [9]. This, too,

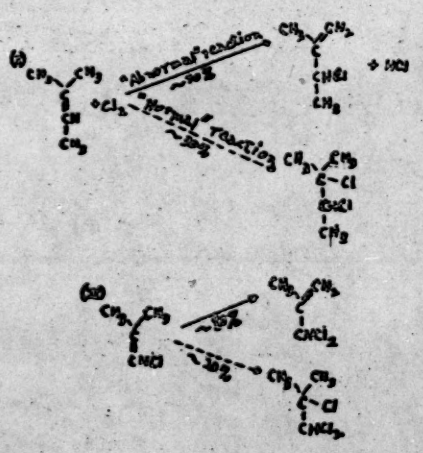
requires complicated refining of the alcohols to eliminate the oxidation by-products, and selenium anhydride is expensive and poisonous. Hence, this method is also hardly usable, even in the laboratory.

It follows from what has been said above, and from other reports in the literature, that up to the present time we have no general methods for producing all sorts of terpene derivatives (alcohols, aldehydes, ketones, halohydrins, acids, etc.) with the same structure and degree of saturation as the initial terpene – methods that are cheap and convenient and yield individual substances rather than mixtures that are hard to separate.

II

All the known terpenes, the open-chain as well as the cyclic ones, with the sole exceptions of bornylene and the rare γ-pinene, are homologs of the simplest ethylene hydrocarbons with a branched double bond: isobutylene (such as camphene, β-pinene, α- and β-fenchenes); trimethylene (such as myrcene, dipentene, α-terpinene, α-pinene, and carene); and tetramethylethylene (such as terpinolene and β-pyronene).

In the eighties of the last century, M.D.Lvov and his pupils showed that when chlorine is reacted with isobutylene, trimethylethylene, or tetramethylethylene, the reaction products include – beside the "normal" reaction product: the saturated dichloride and the by-products – an "abnormal" product: the unsaturated monochloride with the chlorine not attached at the double bond [10] Their data did not enable them to give a general equation for these transformations or to propose a single mechanism for them. I have made a thorough study of these reactions with several hydrocarbons and chlorides of the ethylene series with a branched double bond, showing that they always yield an ethylene chloride with a shifted double bond [11] (see I).



American researchers, making a study of the formation of unsaturated monochlorides by the chlorination of normal olefins at high temperatures [12], have concluded that these monochlorides are formed by the direct substitution of chlorine for hydrogen without any shift in the double bond, citing in confirmation of this assertion the example of isobutylene, which reacts with chlorine to form an (apparent) substitution product at low temperatures. As it happens, the example of isobutylene is inappropriate, in view of its symmetrical structure; both direct substitution and the action of chlorine result, according to our diagram, in the formation of the same product – chloroisobutylene. The result of the reaction of isocrotyl chloride with chlorine (see II above) corroborates the inappropriateness of that example, as do several other reactions explored by us [11]. The

Americans later accepted our viewpoint regarding the mechanism and the conditions required for accomplishing the reaction in question [13]; when chlorine reacts with olefin whose molecules possess a branched double bond, the halogen is polarized, its positive part being the first to react, attaching itself to the negatively polarized end of the double bond, the liberated chlorine anion captures the most highly protonized hydrogen atom in the vicinity of the double bond, forming hydrogen chloride (shift of the double bond, the "abnormal" reaction), or it is added to the positively polarized end of the double bond, giving rise to the saturated dichloride (the "classical" reaction). This "classical" reaction is of subordinate significance, owing to steric hindrances.

As has been stated above, nearly all the terpenes are analogs of the olefins with a branched double bond, we should therefore expect that their reaction with chlorine is a special case of the M.D.Lvov reaction, taking place - according to the diagram suggested by us - with the principal reaction products being unsaturated monochlorides of the terpenes, with a shifted double bond but with the same degree of saturation and the same carbon skeleton as in the initial terpenes; they are monochlorides of the allyl type, which can enter into all sorts of anion-exchange reactions. Consideration of the available data on the action of chlorine upon the terpenes does not permit of such an inference.

Naudin [14] reacted chlorine with α-pinene and concluded that he had synthesized the dichloride, which decomposed upon heating into cymene and hydrogen chloride. Aschan [15] repeated Naudin's research, reacting 25 g of chlorine with 50 g of α-pinene at temperatures below 0° and recovering an unanalyzed liquid fraction, isobornyl chloride, and a solid dichloride (the latter totaling no more than 15% by weight of the reaction products), to which he attributed the structure of 2,6-dichlorocamphane. Brus [16] also investigated the reaction of chlorine with α-pinene, apparently employing an excess of chlorine, and recovered "bornyl chloride, liquid dichlorides, a solid dichloride with a m.p. of 170°, tricyclene chloride, and polychlorides." Brus [17] also reacted an unstated quantity of chlorine with β-pinene at −15°, recovering nothing but bornyl chloride in the individual state from the reaction product, and gave the following as his explanation of why it was impossible to isolate the crystalline saturated dichloride that he thinks is formed in this reaction: when chlorine reacts with β-pinene, a new center of asymmetry appears in the resulting dichloride (at C_1), which governs the formation of diastereoisomers and hampers crystallization. Langlois [18] reacted chlorine with camphene and fractionated the reaction product at 10 mm; for some reason or other he heated the 95-105° fraction for 5 hours to 190° with an excess of dimethylaniline and secured an unspecified yield of camphene and ω-chlorocamphene. Semmler [19] describes the action of chlorine upon camphene literally as follows: "If chlorine is reacted with 10 g of camphene in glacial acetic acid, the first thing that happens is substitution; the whole mixture heats up considerably if no chilling is provided beforehand. The reaction ends within about 20 minutes. After being poured into water, alkalinized, and extracted with ether, all the reaction product passes into the ether. The first distillate to pass over during vacuum distillation is a small amount of first runnings, followed by the main fraction with a b.p. of 130-135° at 10 mm, m.p. 135°, composition $C_{10}H_{15}Cl_3$. Besides this trichloride, which is apparently chlorocamphene dichloride, $C_{10}H_{15}Cl \cdot Cl_2$, we also recover chlorocamphene, $C_{10}H_{15}Cl$, and $C_{10}H_{15}Cl \cdot HCl$."

We cite this extract deliberately, for it is typical of the style and quality of the papers on the reaction of chlorine with the terpenes that have been published up to the present time. All the authors note the evolution of abundant

quantities of hydrogen chloride but take no steps to bind it or to eliminate it, so that the HCl reacts with the terpenes and chlorides, resulting in unnecessary complications of the mixture of reaction products. None of the authors makes an attempt to discover the initial picture of the reaction by using, as they should have done, an insufficient quantity of chlorine to prevent any interaction between it and the accumulating initial products. All the authors try to obtain crystalline dichlorides (the "classical" reaction), often paying no attention to the liquid products, though there is no proof that these dichlorides have to be crystalline. By heating camphene chloride with dimethylaniline, Langlois precluded any possibility of isolating all the initial reaction products, as has been shown above. As is seen from what has gone before, we are totally unable, at the present time, to deduce any unified diagram of the action of chlorine upon the terpenes from the data in the literature, [20,21].

We are entirely justified in asserting that the researches described have not shed any light, but have rather clouded the picture of the reaction of chlorine with the terpenes, and that the analogy between the structure and the chemical behavior of the terpenes and that of the simplest ethylene derivatives with a branched double bond postulated by us is neither borne out nor refuted by the data in the literature, so that an open field for research lies before us. It should be expected that reacting terpenes with chlorine under the conditions employed by us to chlorinate the olefins [11] (deficiency of chlorine, chilling and stirring, binding the HCl with sodium bicarbonate, avoiding overheating, etc.) will enable us to shed light upon the initial stage of the reaction and to prove the postulated analogy.

III

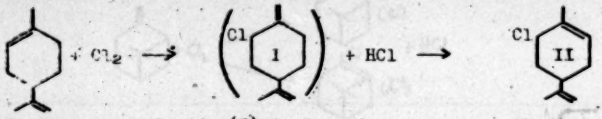
The structure of the terpenes is much more varied and complex than that of quaternary olefins. The terpenes include such structural elements as rings of various sizes and cyclic and semicyclic double bonds, which do not exist in the olefins. The rules governing the formation of allylic monochlorides established by us for quaternary olefins, compared with the known properties of cyclic compounds, especially the terpenes, enable us to make several predictions concerning the likely structure of the conjectured products of the reaction of the terpenes with chlorines, as well as their stability and the direction the transformations will take.

Earlier, using the simplest branched olefins as examples, we demonstrated that, with all other conditions remaining the same, the yield of the "abnormal" reaction will be greater whenever the nascent chlorine anion can capture hydrogen in the form of a proton from the methyl group adjacent to the double bond, instead of from the methylene group. We ascribed this fact to the high "protonicity" of the hydrogen in the first instance, as compared with the second instance, as based upon the concept of the inductive effect [11]. At the present time we have experimental proof that methylic hydrogen in the olefins possesses higher acidity than methylenic or methynic hydrogen [22], which quite independently corroborates our suggested mechanism for the "abnormal" Lvov reaction and entitles us to apply these considerations to other cases as well. Now let us examine the possible reactions of chlorine with various terpenes from this point of view.

1) Open-chain terpenes (ocimene, allo-ocimene, and myrcene) are complete analogs of the branched olefins, with one exception: they possess conjugated double bonds. Hence, in this case the basic factor requiring clarification is whether Thiele's law is applicable or not. We might expect that in this case, too, the "abnormal" reaction is the principal one, yielding unsaturated allylic monochlorides

with the composition $C_{10}H_{17}Cl$. For the reasons outlined earlier [11], in myrcene and allo-ocimene, the double bond -Δ^2 should first react with chlorine. The resulting $C_{10}H_{15}Cl$ monochlorides ought to polymerize readily, like the open-chain terpenes, and be thermally unstable substances that liberate hydrogen chloride readily.

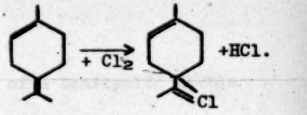
2) Monocyclic terpenes. When dipentene is reacted with chlorine, the -Δ^1 double bond ought to be the first to react (maximum branching [11]). The reaction is as follows:

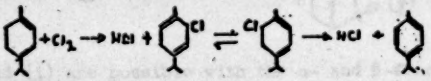


but it is unlikely that the chloride (I) is formed, inasmuch as the formation of a semicyclic double bond requires 5-7 cal per mol, and the double bond is shifted around the ring, the chloride (II) being formed.

In terpinolene, the -$\Delta^{4,8}$ double bond ought to be the first to react. The resulting tertiary monochloride must not polymerize, inasmuch as isomerization results in the formation of a semicyclic double bond, which entails an appreciable loss of energy.

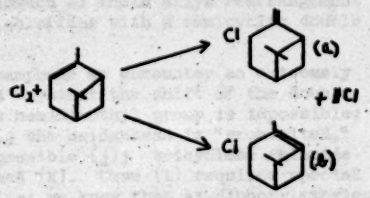
According to what has been set forth above, in α-terpinene, the principal reaction ought to be an "abnormal" 1,4-addition reaction – a side reaction. First, the double bond ought to react, (equal branching of both bonds, a methyl group attached at the -Δ^1 bond, and an isopropyl and a methylene group attached at the -Δ^3 bond). The resulting monochloride ought to be unstable, liberating hydrogen chloride and forming p-cymene, which involves a considerable gain in energy [24] ("aromatization" of the ring), amounting to some 20 Cal per mol. These transformations may be represented by the following diagram:

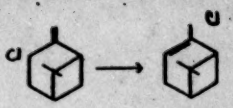




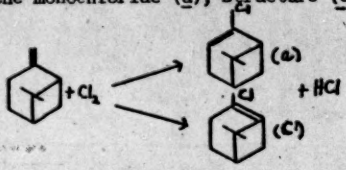
3) In the bicyclic terpenes, the prohibition of the formation of semicyclic double bonds is reinforced by the "Bredt interdiction," the difficulty of forming a double bond at the bridgehead (the point where two rings are joined) [25], owing to the steric hindrances that intervene. In α-pinene we are faced with both of these two prohibitions. Both of the possible structures for the monochloride are "forbidden."

Structure (a) is more probable, since the work involved in forming a semicyclic double bond is doubtless less than the work required to form a double bond at the bridgehead, and the hydrogen in the methyl group is more protonic than that in the methyne group. However, Structure (a) must be unstable and must undergo an allyl rearrangement (see below) to a stabler structure without a semicyclic double bond.

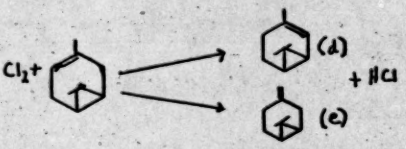




β-Pinene must yield the monochloride (a); Structure (c) is "forbidden":

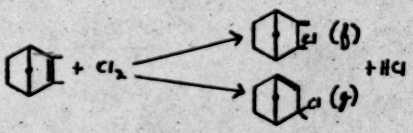


Δ^3-Carene must yield the chloride of Δ^4-carene:

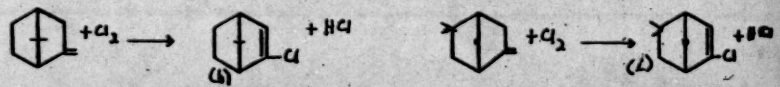


inasmuch as Structure (e) is "forbidden" by the formation of a semicyclic double bond.

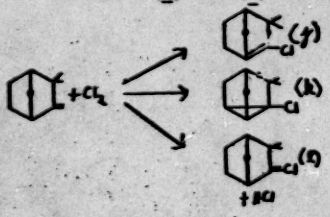
Only one initial product (f) is possible with santene; the (g) chloride is "prohibited" by Bredt's law.



Chlorides (h) and (i) are possible with the α- and β-fenchenes:



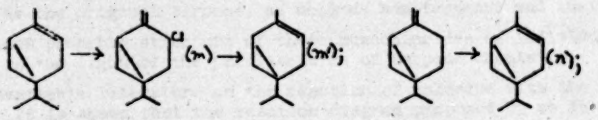
Chlorides with the double bond at the end of the bridge are "prohibited". The chlorides (h) and (i) must be stable, inasmuch as their allyl rearrangement results in chlorides with a semicyclic double bond.



In camphene we encounter an extremely "prohibited" system: the shift of the double bond to the hemidimethyl group is impossible; its shift to the bridgehead is "prohibited," but not impossible (j); tricyclene chloride may be formed (k). Case (l) requires special consideration: we know that as-diphenylethylene, when reacted with bromine, yields 2-bromo-1,1-

-dimethylethylene, i.e., the bromine anion captures the hydrogen of the methylene group, for lack of any other possibility. In Case (l), the hydrogen atoms of the methylene group, after the chlorine atom has attached itself to their carbon atom, are "protonized" by the chlorine atom's negative inductive effect and can then combine with the chlorine anion to form a mol of HCL. This reaction is hampered by the like signs of the charges on the chlorine atom that is attached to the methylene group and on the anion, but any other variant of the "abnormal" reaction is likewise hampered in this instance, and hence this "abnormal" reaction must exhibit a lower yield than that obtained with the other terpenes. In the chlorides (j) and (k), the chlorine must be mobile, and this is why Langlois (see above) was able to secure at best only the chloride (l) with an immobile atom when he heated a mixture of chlorides with dimethylaniline to a high temperature for a long time. It is more likely that he secured this chloride by splitting hydrogen chloride from the saturated camphene dichloride.

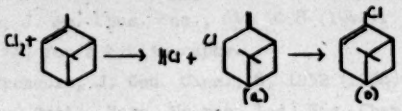
With α-thujene and sabinene only the chlorides (m) and (n) are possible:



other structures are "prohibited" by Bredt's law. The chloride (m) must be readily isomerized to the chloride (m'), the semicyclic double bond disappearing.

IV

Halides of the allyl type are unstable substances that can undergo the so-called allyl rearrangement. This latter has been known for some time [28] as far as the bromides are concerned. We have described the corresponding behavior of the aliphatic monochlorides and dichlorides [27] and have shown that they, too, are thermally unstable, being rearranged, reversibly or irreversibly, into their allylic isomers when heated above 70-80°. We explained the reasons for the reversibility or irreversibility of the rearrangement of allylic dichlorides. The allylic monochlorides of the terpenes that we are concerned with must likewise be capable of allyl rearrangement when heated, and, as stated above (Section III), this rearrangement must be irreversible if there is a semicyclic double bond in the allylic system. Hence the terpene monochlorides must be separated from the reaction mixture at temperatures that do not exceed 60° or so; otherwise, false conclusions may be reached regarding the structure of the initial products of the reaction of chlorine with the terpenes, and the reaction equation proposed by us may be "disproved," as is evidenced by the following example:



The chloride (o) is the product of an apparent substitution of chlorine for hydrogen in the methyl group of α-pinene, and acknowledging it to be the initial reaction product resuscitates the "substitution theory" of the American school.

SUMMARY

1. An analogy is postulated between the chemical behavior of the simplest olefins with a branched double bond and the terpenes.

2. With this analogy as a foundation, an equation is proposed for the reaction of chlorine with the terpenes; the initial products of this reaction must be monochlorides of the allylic type with a transposed double bond of the same degree of unsaturation and the same carbon skeleton as in the original terpene of the $C_{10}H_{15}Cl$ series (principal reaction), plus more highly saturated dichlorides of the $C_{10}H_{18}Cl_2$ series (side reaction).

3. Owing to the existence of a mobile, allylic chlorine atom in these monochlorides, they must be able to enter into varied anion-exchange reactions, which opens up the feasibility, in principle, of developing universal methods of synthesizing terpene derivatives with the same carbon skeleton and the same degree of unsaturation as the original terpene, as well as homoterpenes and their derivatives.

4. The most probable structure of these monochlorides of individual terpenes is discussed in the light of the peculiarities of terpene chemistry.

5. The available literature on the reaction of chlorine with the terpenes is examined. It is shown that the reaction diagram proposed by us is not corroborated by the data in the literature, nor is it refuted by these data. It is shown that elementary errors in method and setup and execution of the published researches made it impossible for their authors to discover the initial stage of the action of chlorine upon the terpenes or to supply the general pattern of this reaction. The conditions necessary for securing the initial products have been elaborated, and the mechanism of the reaction in question has been ascertained.

LITERATURE CITED

[1] Soden, Elze, Chem. Ztg., 29, 1031 (1905).

[2] Blumann, Lieb. Ann., 478, 303 (1930).

[3] Wallach, Lieb. Ann., 346, 229 (1906).

[4] Blumann, Ber., 47, 2628 (1914).

[5] Blumann, Ber., 46, 1194 (1913).

[6] Schmidt, Ber., 63, 1130 (1930).

[7] Blumann, Ber., 47, 2623 (1914).

[8] Weinhaus, Lieb. Ann., 439, 20 (1924).

[9] Palkin, J. Am. Chem. Soc., 64, 1008 (1942).

[10] See [11] for a bibliography.

[11] D.Tishchenko, J. Gen. Chem., 8, 1232 (1938).

[12] Burgin, Groll, Engs, Hearne, Ind. Eng. Chem., 31, 1413 (1939).

[13] Burgin, Hearne, Rust, Ind. Eng. Chem., 33, 384 (1941).

[14] Naudin, Bull. Soc. Chim., (2) 37, 111 (1882).

[15] Aschan, Ber., 61, 38 (1928).

[16] Brus, Comptes rendu., 180, 1507 (1925).

[17] Brus, Comptes rendu., 186, 1507 (1928).

[18] Langlois, Ann. Chim., 12, 282 (1919).

[19] Semmler, Ber., 35, 1020 (1902).

[20] Simonsen, Terpenes, Vol. I. State Light Industry Press, 1936, p. 127.

[21] Wallach, Lieb. Ann., 264, 32 (1891); 270, 196.

[22] Morton, J.Am. Chem. Soc., 67, 2224 (1945).

[23] See, for example: G.Wittig, Stereochemie, Leipzig, 1930, page 154.

[24] Roth, Lieb. Ann., 407, 145 (1915).

[25] Bredt, Lieb. Ann., 395, 26 (1913).

[26] Claisen, J. prak.Chem., 105, 65 (1922).

[27] D.Tishchenko, J. Gen. Chem., 6, 1549 (1936); 8, 1237 (1938); 7, 658 (1937).

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THE STRUCTURE OF THE SALTS FORMED FROM ALIPHATIC DIAMINES AND DICARBOXYLIC ACIDS

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Not much attention has been paid in the literature up to the present time to the structure of the salts of aliphatic diamines and dicarboxylic acids, which are used as the raw materials for the production of polyamide resins and fibers [1]. Korshak and Rafikov [2] touched upon this problem in one of their papers, concluding that of the possible structures for hexamethylenediamine adipate:

$$(I)\quad {}^{+}NH_3 - R - NH_3^{+}$$
$$\quad\quad {}^{-}OOC - R_1 - COO^{-}$$

$$(II)\quad \ldots\ {}^{+}NH_3 - R - NH_3^{+} \cdot {}^{-}OOC - R_1 - COO^{-} \cdot {}^{+}NH_3 - R - NH_3^{+} \ldots$$

Formula (II) is to be preferred, since the viscosity of solutions of this salt indicate that its molecules are associated linearly.

These are not the only possible variants for the structure of hexamethylenediamine adipate, inasmuch as adipic acid and hexamethylenediamine belong to the bifunctional weak acids and bases whose dissociation constants are quite close to one another (Table 1); the structure expressed by the formula:

$$NH_2 - R - NH_3^{+} \cdot {}^{-}OOC - R - COOH,$$

is obviously improbable for salts of this type.

The dissociation constants of some aliphatic dicarboxylic acids and diamines are listed in Table 1. We could not find the value of K_2 for the diamines in the handbooks. Nor were we able to find values for either K_1 or K_2 for hexamethylenediamine. To judge from the figures given for the other diamines, it must be supposed that they are negligibly small.

We were interested in checking the structure of hexamethylenediamine adipate by other methods as well, and in ascertaining the structure of salts of different compositions, formed from various aliphatic diamines and dicarboxylic acids.

The diamines we employed were hexamethylenediamine and ethylenediamine; the

TABLE 1

Bifunctional compound	Temperature	Dissociation constant
Adipic acid	25°	K_1 3.26 x 10^{-5} [4]
	100	K_2 2.4 x 10^{-6} [5]
Succinic acid	25	K_1 6.65 x 10^{-5} [6]
	25	K_2 2.7 x 10^{-} [7]
Oxalic acid	25	K_1 3.8 x 10^{-2} [7]
	25	K_2 3.0 x 10^{-5} [8]
Ethylenediamine	25	8.5 x 10^{-5} [9]
Tetramethylenediamine	25	5.1 x 10^{-4} [9]
Pentamethylenediamine	25	7.3 x 10^{-4} [9]

acids were adipic, succinic, and oxalic acids.

Salts were prepared from various combinations of these constituents, one of the reagents sometimes being taken in large excess over the other in the preparation of some samples, in addition to the samples prepared with equimolecular proportions of the reagents.

The salts were crystallized from water-alcohol solutions (80% ethyl alcohol); after recrystallization, their melting points did not vary by more than 1° as a rule. Inasmuch as dicarboxylic acids dissolve with difficulty in alcohol, the diamines, which dissolve readily in alcohol even at room temperature, were used as the excess reagent to avoid difficulties in purifying the salt samples. If Formula (II) is correct, the excess of the diamine ought to result in formation of a compound of the following composition:

$$H_2N - R - \overset{+}{N}H_3 \cdot \overset{-}{O}OC - R_1 - \overset{-}{C}O\overset{-}{O} \cdot \overset{+}{N}H_3 - R - NH_2.$$

Analysis of the synthesized salts indicated that excessive quantities of hexamethylenediamine or of ethylenediamine do not affect the composition of the salts, which always contained equimolecular quantities of the reagents (with the exception of the salts prepared from oxalic acid and the diamines). Salts of this kind can have nothing but a cyclic structure, and hence Formula (I) applies to them.

The quantity of diamine used had no effect upon the composition of the salts in which the acid component was oxalic acid. In every case – both when equimolecular proportions were used and when the diamines were reacted with the oxalic acid in a 2:1 molar ratio – it was found that the salts contained 2 mols of oxalic acid per mol of the diamine. Hence, oxalic acid differs from adipic and succinic acids in that it forms acid rather than neutral salts with the aliphatic diamines.

In view of the fact that the ratio of the dissociation constants is much higher in the case of oxalic acid than in the dicarboxylic acids of high molecular weight, the synthesis of acid hexamethylenediamine and ethylenediamine oxalates from solutions containing an excess of the diamine is not surprising. Whereas a low value of the K_1/K_2 ratio (it is about 20 for succinic acid [3]) indicates a negligible difference in the activity of the funtional groups in bifunctional compounds and agrees with the appearance of salts such as hexamethylenediamine

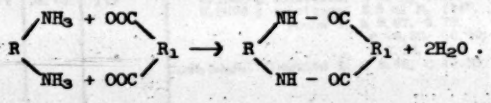
succinate, a high value of the K_1/K_2 ratio (this is as high as 1269 in the case of oxalic acid [3]), which is characteristic of a difference in functional activity, must lead to the formation of compounds with a different structure – of the type of the acid hexamethylenediamine oxalate (Table 2).

Hence, although the structure of salts formed from oxalic acid and the diamines is not cyclic, it does not conform to Formula (II), which presupposes a neutral rather than an acid salt. The data in the literature on the composition of hexamethylenediamine oxalate [10] and ethylenediamine succinate [11] agree with ours (Table 2).

The nature of the processes taking place during the formation of polyamide resins is usually bound up with the structure of their initial products. Thus, the resin of ε-caprolactam, which has a cyclic structure, is a product formed as the result of an additive process (polymerization), whereas the assumed linear structure of the molecules of the salts of diamines and dicarboxylic acids justifies us in the belief that the process of formation of a polymer from them is of a condensation nature.*

The cyclic structure of the salts used as the raw materials for the production of polyamide resins, demonstrated in the present paper, eliminates any reason for restricting the mechanism of the reactions resulting in the formation of polymers to ε-caprolactam and the salts mentioned above.

This follows from a consideration of the reaction in question with salts of cyclic structure. The first stage of this reaction must take place according to the following equation:



Inasmuch as the structure of the resulting product is quite close to that of ε-caprolactam, the mechanism of the subsequent reactions must be similar for the two of them.

EXPERIMENTAL

Synthesis of hexamethylenediamine adipate, with equimolar proportions of the initial products. 0.58 part by weight of hexamethylenediamine and 0.73 part by weight of adipic acid were placed in ethyl alcohol diluted with water – 5.5 parts by weight of 95% ethyl alcohol and 0.89 part by weight of water.

The mixture was heated until the solution became transparent. After the latter had cooled, crystals of the salt settled out; they were filtered out, washed with alcohol, and recrystallized from ethyl alcohol diluted with water. Salts with a 2:1 molar ratio of hexamethylenediamine to adipic acid, as well as several other salts, the analysis of which is given in Table 2, were prepared in the same manner.

Acid hexamethylenediamine oxalate was prepared in the same way as hexamethylenediamine adipate.

*V. V. Korshak and S. P. Rafikov, Synthesis and Analysis of high-molecular Compounds. USSR Academy of Sciences Press, 1949.

TABLE 2

No.	Composition of salt	Molar ratio	Salt yield (% theory)	M.p. of salt	Analysis of salt	Salt formula
1	Hexamethylene-diamine Adipic acid	1:1	88.08	190-191°	0.1100 g substance: 9.9 ml N_2 (15°; 762 mm) 0.1022 g substance: 9.5 ml N_2 (15°; 759.4 mm) Found %: N 10.58; 10.897; C 54.56; H 10.04. $C_{12}H_{28}O_4N_2$. Computed %: N 10.687; C 54.96; H 9.92	$^{+}H_3N-(CH_2)_6-NH_3^{+}$ $^{-}OOC-(CH_2)_4-COO^{-}$
2	Same as in No. 1	2:1	78.72	190-191	0.104 g substance: 10.6 ml N_2 (16°, 738.9 mm) 0.100 g substance: 10.0 ml N_2 (16°, 738.6 mm) Found %: N 10.58, 10.38; C 54.7 . 54.80; H 9.98, 9.90 $C_{12}H_{28}O_4N_2$. Computed %: (vide supra)	Same as in No. 1
3	Hexamethylene-diamine Succinic acid	1:1	83.09	191-192	0.1012 g substance: 10.9 ml N_2 (16°, 764 mm 0.1120 g substance: 11.6 ml N_2 (16°, 764 mm Found %: N 11.76, 11.76; $C_{10}H_{22}O_4N_2$. Computed %: N 11.97; C 51.28; H 9.40	$^{+}H_3N-(CH_2)_6-NH_3^{+}$ $^{-}OOC-(CH_2)_2-COO^{-}$
4	Same as in No. 3	2:1	82.49	191-192	0.100 g substance: 10.5 ml N_2 (14°, 744 mm) 0.1012 g substance: 10.4 ml N_2 (14° 752.1 mm) Found %: N 12.16, 12.01; C 50.94; H 9.22 $C_{10}H_{22}O_4N_2$. Computed %: vide supra.	Same as in No. 3
5	Hexamethylene-diamine Oxalic acid	1:1	84.65	177	0.1000 g substance: 8 ml N_2 (15°, 785.5 mm) 0.1000 g substance: 8.5 ml N_2 (14°, 740 mm) Found %: N 9.07, 9.79; C 40.89, 40.90; H 7.20, 7.10 $C_8H_{20}O_4N_2$. Computed %: N 9.46; C 40.53; H 6.76	$^{-}HOOC-COO^{-}H_3N(CH_2)_6$ $^{+}NH_3.OOC-COOH$
6	Same is in No. 5	2:1	86.15	177	0.1000 g substance: 8.3 ml N_2 (16°, 746.9 mm) 0.1000 g substance: 8.0 ml N_2 (16°, 753.9 mm) Found %: N 9.56, 9.29; C 40.92; H 6.98 $C_8H_{20}O_4N_2$. Computed %: (vide supra)	Same as in No.5
7	Ethylene-diamine Adipic acid	1:1	88.06	130-131	0.1000 g substance: 11.3 ml N_2 (16°, 765.9 mm) 0.1000 g substance: 12.0 ml N_2 (16°, 755.9 mm) Found %: N 13.46, 13.71; C 46.24, 46.50; H 8.99, 9.02 $C_8H_{18}O_4N_2$. Computed %: N 13.59; C 46.60; H 8.74	$^{+}H_3N-(CH_2)_2-NH_3^{+}$ $^{-}OOC-(CH_2)_4-COO^{-}$
8	Same as in No. 7	2:1	87.69	130-131	0.1000 g substance: 11.9 ml N_2 (16°, 754 mm) 0.1030 g substance: 12 ml N_2 (16°, 759.4 mm) Found %: N 13.83, 13.64; C 46.72; H 9.12 $C_8H_{18}O_4N_2$. Computed %: (vide supra)	Same as in No.7.
9	Ethylene-diamine Succinic acid	1:1	85.17	Decomposition at 190°	0.1000 g substance: 13.3 ml N_2 (16°, 759.4 mm) 0.1200 g substance: 16.1 ml N_2 (16°, 757.1 mm) Found %: N 15.57, 15.68; C 40.58, 40.68; H 8.00, 8.16 $C_6H_{14}O_4N_2$. Computed %: N 15.73; C 40.45; H 7.87	$^{+}NH_3-(CH_2)_2-NH_3^{+}$ $^{-}OOC-(CH_2)_2-COO^{-}$
10	Same as in No. 9	2:1	83.99	"	0.1000 g substance: 13.4 ml N_2 (16°, 753.1 mm) 0.1060 g substance: 16.1 ml N_2 (16°, 753.2 mm) Found %: N 15.45, 15.48; C 40.72; H 8.1. $C_6H_{14}O_4N_2$. Computed %: (vide supra)	Same as in No. 9

TABLE 2 (continued)

No.	Composition of salt	Molar ratio	Salt yield (% theory)	M.P. of salt	Analysis of salt	Salt formula
11	Ethylene-diamine Oxalic acid	1:1	87.23	Decomposition at 205°	0.1030 g substance: 10.5 ml N_2 (15°, 753.1 mm) 0.1072 g substance: 10.8 ml N_2 (16°, 757.2 mm) Found %: N 11.8; C 29.94; H 5.48 $C_6H_{12}O_8N_2$ Computed %: N 11.67; C 30.0; H 5.0	$^{-}HOOC\text{-}COO^{+}H_3N\text{-}(CH_2)_2\text{-}NH_3^{+}\text{-}OOC\text{-}COOH^{-}$
12	Same as in No. 11	2:1	84.40	"	0.1022 g substance: 10 ml N_2 (16°, 761 mm) 0.1030 g substance: 10.3 ml N_2 (16°, 759.2 mm) Found %: N 11.36, 11.61; C 30.31, 30.12; H 5.24, 5.32. $C_8H_{12}O_8N_2$. Computed %: (vide supra)	Same as in No. 1

SUMMARY

1. Salts of aliphatic diamines and dicarboxylic acids have a constant composition, no matter what the molar proportions of the reagents used in their preparation; the composition depends largely upon the dissociation constants of the functional groups in the acid component of the salt.

2. Succinic and adipic acid, in which K_1/K_2 is small (≤ 20) owing to the slight difference between the values of the dissociation constants of the functions in every compound, form cyclic neutral salts when reacted with aliphatic diamines.

3. Oxalic acid, in which the dissociation constants of the functional groups are very far apart ($K_1/K_2 = 1269$), forms acid salts with linear structure of the molecules when reacted with aliphatic diamines.

LITERATURE CITED

[1] Kohei Hosino, J.Chem.Soc. Japan, 61, 475-81 (1940); E.I.du Pont de Nemours, Brit. Patent 506125, Chem. Abs., 1939, 9497; E.I.du Pont de Nemours, French patent 845691. Italian Patent 368473.

[2] V.Korshak and S.Rafikov, J.Gen.Chem 14, 976 (1944).

[3] S.Glasstone. The Electrochemistry of Solutions. United Scientific-Technical Press, 1936.

[4] Bokseken, Verkade, Rec.trav.chim., 36, 170 (1917).

[5] Smith, Z. phys. chem., 25, 194 (1898).

[6] Ostwald, Z. phys. Chem., 3, 282 (1889).

[7] Chandler, J.Am.Chem.Soc., 30, 713, 698 (1908).

[8] Datta and Dhar, J.Chem.Soc., 107, 824 (1915)

[9] Bredig, Z. phys. Chem., 13, 191 (1894).

[10] Curtius, Clemm, J. prak. Chem., (2), 62, 205 (1900); (2) 29, 1167 (1884).

[11] Mason, J.Chem.Soc., 55, 10 (1889); Anderlini, Gazz., 24, 1, 398 (1894).

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α,α'-DIMETHYL-β,β'-DIHYDROXYDIETHYLAMINE

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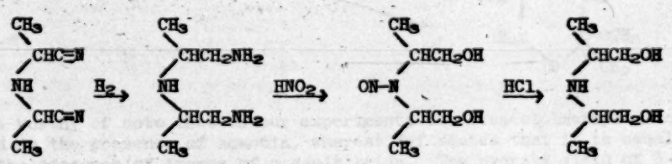
The synthesis of α,α'-dimethyl-β,β'-dihydroxydiethylamine has not been described in the literature up to now. This is apparently due to the fact that most of the aliphatic alkanolamines are usually produced by condensing olefin oxides with ammonia or with amines, the hydroxyl group being formed with the least hydrogenated hydrogen atom. In fact, as Krasusky [1] has pointed out, it is easy to produce the isomeric β,β'-dimethyl-β,β'-dihydroxydiethylamine by reacting propylene epoxide with ammonia.

We tested several possible variants of synthesizing α,α'-dimethyl-β,β'-dihydroxyethylamine. One of the ways of synthesizing this compound seemed to us to be the reduction of α,α'-dicyandiethylamine (I) to the corresponding triamine (II), followed by conversion of the latter into a dihydroxy compound by reacting it with HNO_2, as follows:



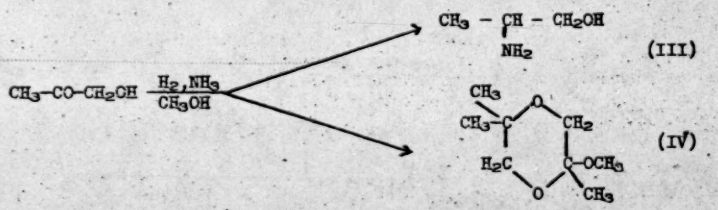
(I) (II)

To carry out the first stage, we employed both catalytic hydrogenation, which is often used to reduce special nitriles [2], and a Ladenburg reduction. Catalytic hydrogenation was carried out at a pressure of 15 atm in the presence of ammonia and of a Rainey nickel catalyst. Under these conditions no hydrogen was absorbed, either at room temperature or when heated to 60°. In the Ladenburg reduction we succeeded in securing a small quantity of a liquid substance with the characteristic odor of an amine; analysis of its picrate indicated that it apparently was the expected α,α'-dimethyl-β,β'-diaminodiethylamine. The yield of this base was so negligible, however, that it was impracticable to employ it as the initial material for synthesizing the dialkanolamine.

The synthesis of amines by reductive amination of carbonyl compounds is well known in the literature. Skita and Keil [3], and later Couturier [4], have shown that hydroxycarbonyl compounds may also undergo reductive amination, giving rise to the corresponding amino alcohols. We tried to effect the reductive amination

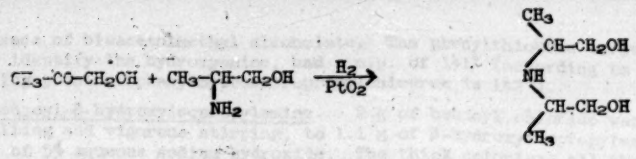
of acetol with ammonia in the expectation that this reaction would yield, besides the primary β-hydroxyisopropylamine, the secondary dialkanolamine with the desired structure. The first catalyst employed was platinum oxide, prepared by the Adams method, but this did not result in the absorption of any hydrogen, whether at room temperature or at high temperature. Efforts were made to carry out this reaction in the presence of the Rainey nickel catalyst, the use of which for the reductive amination of hydroxy ketones has not been hitherto described in the literature. The reaction was carried out at a hydrogen pressure of 15 atm. Methanol was used as the solvent, based on Nef's assertion [5] that acetol is most stable in this solvent. The excess of ammonia was 20% above the computed quantity.

As a number of experiments has shown, the optimum temperature for this reaction is 80-90°. Hydrogen absorption is slow at lower temperatures: above 100° the reaction products undergo strong tarring. In none of the experiments was hydrogenation carried out to completion, with about 80% of the theoretical quantity of hydrogen being absorbed. The reason for this phenomenon was learned during treatment of the hydrogenation product. We recovered a mixture that was hard to separate, consisting of a liquid base, which was identified as its phenylthiourea derivative and proved to be a monoalkanolamine (β-hydroxyisopropylamine) (III), and a crystalline substance with a m.p. of 126.5-127°, which contained no nitrogen. This agrees with Nef's data [5] for bisacetolmethyl alcoholate (IV) – the product of the condensation of acetol with methanol:



It is worthy of note that in our experiments the bisacetolmethyl alcoholate was formed in the presence of ammonia, whereas Nef states that it is usually produced in the presence of traces of organic acids. The overall yield of β-hydroxyisopropylamine did not exceed 21% of the theoretical. No fraction that contained a dialkanolamine was recovered; a large part of the reaction product consisted of a tar.

We succeeded in synthesizing α,α'-dimethyl-β,β'-dihydroxydiethylamine by the reductive amination of acetol, β-hydroxyisopropylamine serving as the amine in the reaction. The reaction was carried out in absolute methanol at room temperature and atmospheric pressure in the presence of a platinum catalyst. It was found that the reductive amination of acetol with β-hydroxyisopropylamine in the presence of a platinum catalyst yields positive results, wherein it differs from the analogous experiments with ammonia, which were fruitless, as stated above. Formation of α,α'-dimethyl-β,β'-dihydroxydiethylamine takes place under conditions that are so mild as practically to eliminate side reactions due to the instability of acetol. The reaction may be pictured as follows:



The best yield of the dialkanolamine (70%) is obtained with a 50% excess of the hydroxyamine over the computed quantity. The rate at which hydrogen is absorbed depends upon the quality of the catalyst. When a freshly prepared platinum oxide of high enough activity is employed, hydrogenation is completed within 4 hours, most of the hydrogen being absorbed during the first half hour. It should be borne in mind that when hydrogenation takes a longer time, we get – in addition to the desired substances – by-products that are greatly resinified upon exposure to the air, thus hampering the purification of the dihydroxyamine and resulting in a sharp drop in the latter's yield. The method of synthesis set forth may, apparently, be useful for synthesizing other dialkanolamines of this type.

EXPERIMENTAL

Reduction of α,α'-dicyandiethylamine. A solution of 5 g of α,α'-dicyandiethylamine, prepared by the Dubsky method [6], in 300 ml of absolute alcohol was placed in a 1-liter round-bottomed flask fitted with a long reflux condenser. The solution was heated to the boiling point, and 30 g of metallic sodium was quickly added. After the reaction was complete, the solidified mass was diluted with 80 ml of water, the alcohol was driven off over a boiling water bath, and the residue was again diluted with a small quantity of water. The separating upper layer – a slightly yellowish oil – was extracted with ether. After the ether extract had been desiccated with potash and the solvent had been driven off, the residue was distilled in vacuum. This yielded about 0.5 g of a yellowish liquid with the odor of an amine and a b.p. of 62-64° at 12 mm. The substance exhibits an isonitrile reaction for a primary amino group. Endeavors to recover more of the base from the aqueous layer or from the alcoholic distillates were fruitless.

Owing to the small quantity of substance recovered, it was not purified. Its picrate crystallizes as yellow hexahedral prisms with a m.p. of 232° (decomposition).

1.825 mg substance: 0.329 ml N_2 (17°, 744 mm).
Found %: N 20.7.
$C_6H_{17}N_3 \cdot 3HOC_6H_2(NO_2)_3$. Calculated %: N 20.53.

Reductive amination of acetol by ammonia. 39 g of freshly prepared acetol, 83 ml of a 13% solution of ammonia in methanol, and 5 g of a Rainey nickel catalyst in the form of a paste were placed in an oscillating autoclave. The mixture was agitated for 5 hours at 80-90° in a hydrogen atmosphere at 15 atm. After the catalyst had been filtered out, the alcohol was driven off, and the residue was fractionated in vacuum. This yielded a fraction with a b.p. of 70-80° at 17 mm, which was a mixture consisting of a yellowish liquid and a colorless crystalline substance with a m.p. of 126.5-127° (from toluene), which contains no nitrogen.

In its properties and melting point, the latter is identical with bisacetolmethyl alcoholate [5]. The liquid portion of the fraction yielded 8 g of a substance with a b.p. of 70-76° at 15 mm, which proved to be β-hydroxyisopropylamine

with a trace of bisacetolmethyl alcoholate. The phenylthiourea derivative, synthesized to identify the hydroxyamine, had a m.p. of 141° (according to Gabriel [7], the melting point of phenylhydroxyisopropylthiourea is 142°).

N-Benzoyl-β-hydroxyisopropylamine. 2 g of benzoyl chloride was slowly added, with chilling and vigorous stirring, to 1.1 g of β-hydroxyisopropylamine dissolved in 15 ml of 5% aqueous sodium hydroxide. The thick colorless oil that formed at first soon crystallized. The precipitate was filtered out, washed repeatedly with a 5% solution of sodium bicarbonate and then with water, and desiccated in a vacuum exsiccator. The substance recrystallized from hot aqueous alcohol had a m.p. of 104.5-106°. Thin lamellae that dissolve with difficulty in benzene and are insoluble in water.

4.481 mg substance: 0.294 ml N_2 (19.5°, 750 mm).
Found %: N 7.80.
$C_{10}H_{13}O_2N$. Calculated %: N 7.82.

Reductive amination of acetol by β-hydroxyisopropylamine. Platinum oxide prepared by the Adams method (0.18 g of Pt) was placed in 20 ml of absolute methanol and reduced to platinum black. Solutions of 7.4 g of β-hydroxyisopropylamine, prepared by Gabriel's method [7], and 6.2 g of freshly distilled acetol in absolute methanol were added to the resulting catalyst. The mixture was hydrogenated for 4 hours at atmospheric pressure; the rate at which the hydrogen was absorbed was extremely high at first (up to 900 ml in 30 minutes), but then it slowed down. After hydrogenation was complete, the remaining active catalyst was filtered out, the alcohol was driven off in vacuum, and the residue was distilled at reduced pressure. Distillation yielded, in addition to the unreacted excess of β-hydroxyisopropylamine, 7.8 g of α,α'-dimethyl-β,β'-dihydroxydiethylamine as a thick, colorless liquid with a b.p. of 141° at 12 mm. The yield was 70% of the theoretical.

d_4^{16} 1.0146; n_D^{16} 1.4702; MR_D 36.58 $C_6H_{15}O_2N$ Calculated MR_D 36.53.

6.976 mg substance: 5.24 ml 0.01 N H_2SO_4 (Kjeldahl)
Found %: N 10.51.
$C_6H_{15}O_2N$ Calculated %: N 10.52.

The picrate consisted of elongated yellow tetragonal lamellae (from alcohol) with a m.p. of 195-196°.

2.607 mg substance: 0.361 ml N_2 (20.5°, 729 mm).
Found %: N 15.45.
$C_{12}H_{18}O_9N_4$. Calculated %: N 15.46.

SUMMARY

1. Several possible variants of the synthesis of α,α'-dimethyl-β,β'-dihydroxydiethylamine have been tested.

2. A suitable method has been found for synthesizing this substance, involving the reductive amination of acetol by β-hydroxyisopropylamine.

LITERATURE CITED

[1] K.A.Krasusky, J. Gen. Chem., 6, 460 (1936).
[2] W. Huber, J. Am. Chem. Soc., 66, 876 (1944).
[3] Skita, Keil, Ber., 61, 1452, 1682 (1928).
[4] P. Couturier, Comptes rendu., 207, 345 (1938).
[5] J.Nef, Lieb. Ann., 335, 247 (1904).
[6] J. Dubsky, Ber., 49, 1, 1045 (1916).
[7] S. Gabriel, Ber., 49, 1, 2121 (1916).

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THE PROBLEM OF THE CONVERSION OF DERIVATIVES OF THE ETHYLENIC HYDROCARBONS INTO DERIVATIVES OF THE SIMPLEST POLYMETHYLENIC RINGS

III. THE REACTION OF METHYLPHENYLCYCLOPROPYLCARBINOL WITH HYDROCHLORIC AND SULFURIC ACIDS

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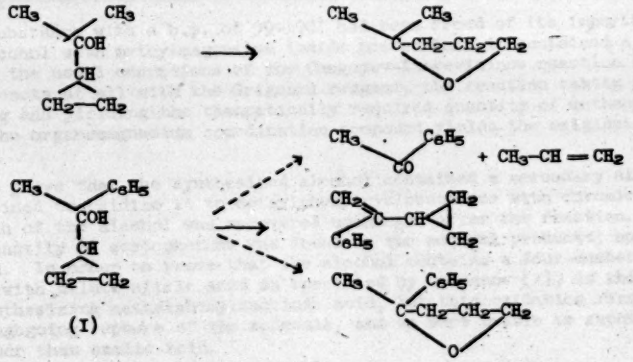
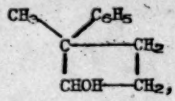
It is known that tertiary alcohols with cyclopropyl radicals – dimethyl- [1] and methylethylcyclopropylcarbinols [2] – yield unsaturated chlorides with an open carbon chain when acted upon by hydrochloric acid, these chlorides being converted into the original cyclic alcohols when reacted with alkaline agents. On the other hand, we know that unsaturated tertiary alcohols that contain phenyl and allyl radicals – methylphenyl- and diphenylallylcarbinols – are decomposed into propylene and the corresponding ketone by heating them with sulfuric acid [3].

We were therefore interested in exploring the reactions of hydrochloric and sulfuric acids with an alcohol that contained both the phenyl and the cyclopropyl radicals, such as methylphenylcyclopropylcarbinol (I), and in finding out what unsaturated chloride would be produced in this reaction, as well as whether it is cyclized by an alkali and whether the action of sulfuric acid upon this alcohol will cause ketonic cleavage. Besides the phenomenon of ketonic cleavage, the action of sulfuric acid upon (I) might be expected to cause dehydration of this alcohol, giving rise to phenylcyclopropylethylene, which N.M.Kizhner [4] produced by reacting acetic anhydride with it. Sulfuric acid might also be expected to isomerize (I), forming the γ-epoxide of 1,1-methylphenyltetramethylene, as N.D. Zelinsky [5] synthesized a γ-epoxide, which he called hexylene epoxide, by reacting oxalic acid with dimethylcyclopropylcarbinol:



(I)

Lastly, we might likewise expect the conversion of (I) into methylphenylcyclobutanol:

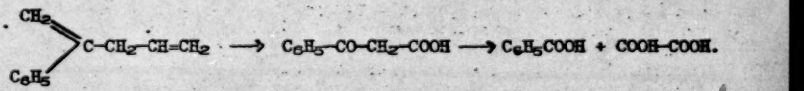


in the same manner as dimethylcyclobutylcarbinol is converted into dimethylcyclopentanol by the action of sulfuric acid [6].

The carbinol (I) was synthesized by the action of phenylmagnesium bromide upon acetyltrimethylene, the reaction being carried out in one phase in absolute ether. The same results were obtained when this alcohol was heated with either 25% or 50% sulfuric acid: in each case the reaction took two paths: dehydration of (I) and its isomeric transformation into a secondary alcohol – methylphenylcyclobutanol. But the dehydration product is not the phenylcyclopropylethylene synthesized by N.M.Kizhner by reacting (I) with acetic anhydride; the action of sulfuric acid gives rise to a diene hydrocarbon with an isolated system of double bonds: 2-phenylpentadiene-1,4 (V).

The dehydration may also affect the allyl radical, since the reaction of (I) with sulfuric acid yields (in addition to the products specified above) a considerable quantity of tar, which is probably a polymerization product of the 1,3-diene hydrocarbon formed: 4-phenylpentadiene-1,3 (IV).

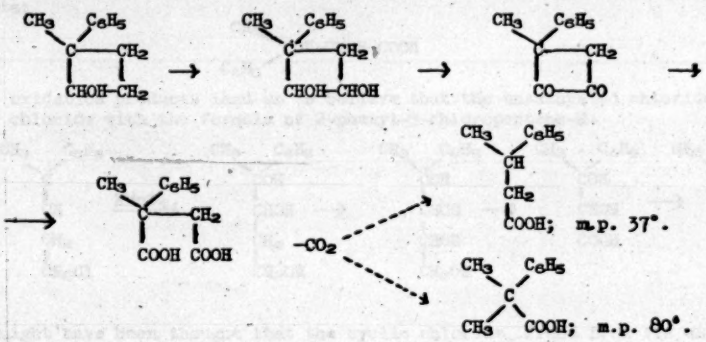
2-Phenylpentadiene-1,4 was present as an impurity in the main reaction product, methylphenylcyclobutanol. This cyclic alcohol, recovered after fractionation of the reaction products, boils at 99-101° and 14 mm and slowly decolorizes a potassium permanganate solution in the cold. After treatment with a $KMnO_4$ solution in the cold, the alcohol boiled at 99-100° and 14 mm and no longer caused any decolorization of a permanganate solution. The oxidation products recovered after this treatment included benzoic and oxalic acids, which can be produced from a hydrocarbon with an isolated system of double bonds:



After the substance with a b.p. of 99-100° had been freed of its impurities, reacting this alcohol with methylmagnesium iodide proved that it contained a hydroxyl group. Under the usual conditions of the Chugayev-Tserevitinov reaction the alcohol hardly reacts at all with the Grignard reagent, the reaction taking place only upon heating and yielding the theoretically required quantity of methane; decomposition of the organomagnesium coordination compound yields the original alcohol again.

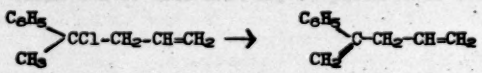
In order to prove that the synthesized alcohol contained a secondary alcohol grouping, we decided to oxidize it to methylphenylcyclobutanone with chromic acid mixture, but much of the alcohol was recovered unchanged after the reaction. Moreover, a small quantity of acetophenone was found in the neutral products; no cyclic ketone was found. In order to prove that the alcohol contains a four-membered ring, it was oxidized with dilute nitric acid as specified by Demyanov [7], in the expectation of synthesizing methylphenylsuccinic acid, but this oxidation resulted in a more thoroughgoing rupture of the molecule, and we were unable to recover any acid product other than oxalic acid.

Only by oxidizing the alcohol with a solution of potassium permanganate and heating the mixture were we able to recover a crystalline acid with a m.p. of 78°. When kept in an exsiccator, this acid changed into a syrupy acid with the formula $C_{10}H_{12}O_2$ This formula and the m.p. of 78° conform to those for dimethylphenylacetic acid, which can certainly be formed from methylphenylcyclobutanol. First this alcohol would have to be oxidized to α,α-methylphenylsuccinic acid, which could be converted into either β-phenylbutyric or dimethylphenylacetic acid by liberating CO_2:



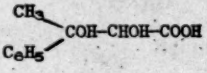
We synthesized dimethylphenylacetic acid, which fused at a considerably lower temperature because it was mixed together with the crystalline acid with a m.p. of 78° that we had synthesized. It suffered no change when kept in the exsiccator. Repeated efforts to analyze the synthesized crystalline acid met with failure, inasmuch as the time required for it to change into a liquid varied considerably: sometimes it would deliquesce within a week, sometimes overnight, while at other times it would be initially recovered as a liquid. When we finally succeeded in roasting it, we found that its composition was the same as that of the liquid acid, $C_{10}H_{12}O_2$. The only remaining hypothesis is that the methylphenylsuccinic acid that is formed liberates CO_2 in both reactions, resulting in a mixture of the acids with melting points of 37 and 78°, which also explains the transformation of their mixture into a syrup.

The reaction of (I) with hydrochloric acid results in the formation of a number of products: a cyclic chloride that contains a trace of an unsaturated chloride; a diene hydrocarbon with isolated double bonds; and a small quantity of a polymer hydrocarbon. The diene hydrocarbon is 2-phenylpentadiene-1,4, as its constants agree wholly with those of the hydrocarbon we recovered in hydrolyzing the chlorohydrin of methylphenylallylcarbinol, whose structure we have proved, and because oxidizing it with a $KMnO_4$ solution yielded benzoic and oxalic acids, i.e., the same result as when we oxidized the hydrocarbon produced by reacting (I) with sulfuric acid. The formation of this hydrocarbon may be pictured as the result of splitting off hydrogen chloride from a chloride of the following structure:

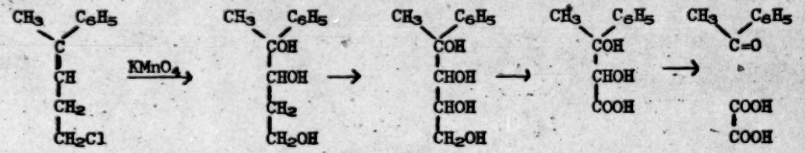


The small quantity of polymer indicates that the detachment of HCl also occurs, in part, otherwise, with the formation of the readily polymerizable 4-phenylpentadiene-1,3.

The trace of the unsaturated chloride was eliminated from the cyclic chloride by treating the latter in the cold with a solution of potassium permanganate. This yielded acetophenone, oxalic acid, and an acid with the formula $C_{10}H_{12}O_4$, which must have the formula of β-phenyl-α,β-dihydroxybutyric acid, according to our experimental data:



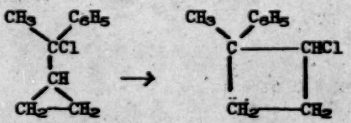
The oxidation products lead us to believe that the unsaturated chloride is a primary chloride with the formula of 2-phenyl-5-chloropentene-2.



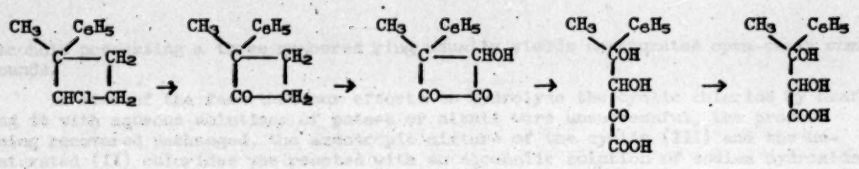
It might have been thought that the cyclic chloride, freed from its unsaturated chloride, would contain a three-membered ring and would be a chlorohydrin of the carbinol (I).

We should then expect that this chloride would be easy to saponify, like a chlorohydrin of a tertiary alcohol. The chloride was recovered unchanged, however, after having been boiled for 150 hours with a 20% solution of potash, as well as after being heated with a 15% solution of NaOH.

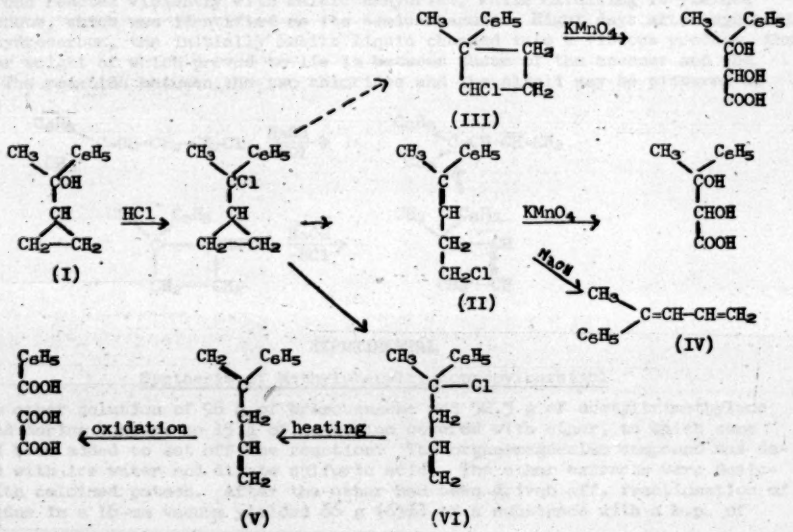
This difficulty encountered in hydrolyzing this chloride forces us to acknowledge that the chloride's structure must be something different, and, as it does not contain a double bond, it must be assumed that the chlorohydrin of carbinol (I) formed in the first stage of the reaction underwent isomerization accompanied by expansion of the ring to a four-membered one and the attachment of a chlorine atom to the ring:



Isomerization resulted in the production of a chlorohydrin of 1,1-methylphenylcyclobutanol-2. That the chloride actually had this structure was confirmed by oxidizing it by heating it to 45-55° with a $KMnO_4$ solution, which yielded the same β-phenyl-α,β-dihydroxybutyric acid as was recovered after oxidizing the unsaturated chloride. The formation of this acid may be pictured as follows:



Summing up all the varied transformations of (I) when acted upon by hydrochloric acid, they may be represented by the following diagram:

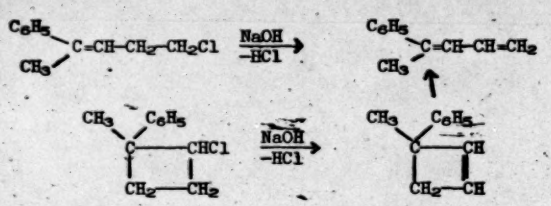


When hydrochloric acid is reacted with (I), the intermediate product is the chlorohydrin corresponding to the original alcohol, with a three-membered ring, which undergoes isomeric conversion at once in two ways: expanding the three-membered ring to a four-membered one (III), and opening the ring, forming two unsaturated chlorides. The first of these (VI), which is the same as the unstable chlorhydrin of methylphenylallylcarbinol we have synthesized [7], was not recovered, as it readily gives off hydrogen chloride, forming two hydrocarbons. The formation of the hydrocarbon (IV) may be judged by the presence of a polymer in the reaction products. Hydrocarbon (V) was recovered, identified, and oxidized to benzoic and oxalic acids. The primary chloride (III) was recovered mixed with a cyclic chloride owing to the closeness of their boiling points; their structures were determined from their oxidation products.

Hence, we have established a very interesting fact: the conversion of a tertiary alcohol of the cyclopropane series into derivatives of cyclobutane when acted upon by hydrochloric and sulfuric acids. The only other known instance of a conversion involving ring expansion is that of a primary alcohol containing a three-membered ring: cyclopropylcarbinol [8]. The action of acids upon tertiary

alcohols possessing a three-membered ring usually yields unsaturated open-chain compounds.

In view of the fact that our efforts to hydrolyze the cyclic chloride by heating it with aqueous solutions of potash or alkali were unsuccessful, the product being recovered unchanged, the azeotropic mixture of the cyclic (III) and the unsaturated (II) chlorides was reacted with an alcoholic solution of sodium hydroxide. This resulted in the liberation of hydrogen chloride by both of the chlorides, each of them yielding the same hydrocarbon, 4-phenylpentadiene-1,3. The synthesized hydrocarbon reacted violently with maleic anhydride, while oxidizing it yielded acetophenone, which was identified as its semicarbazone. Eight days after synthesis of the hydrocarbon, the initially mobile liquid changed into a viscous product, the molecular weight of which proved to lie in between those of the monomer and the dimer. The reaction between the two chlorides and the alkali may be pictured as follows:



EXPERIMENTAL

Synthesis of Methylphenylcyclopropylcarbinol

An ether solution of 98 g of bromobenzene and 52.5 g of acetyltrimethylene was added during 4 hours to 15 g of magnesium covered with ether, to which some CH_3I had been added to set off the reaction. The organomagnesium compound was decomposed with ice water and dilute sulfuric acid. The ether extracts were desiccated with calcined potash. After the ether had been driven off, fractionation of the residue in a 16-mm vacuum yielded 66 g (65%) of a substance with a b.p. of 119-121°.

d_4^0 1.0392; d_4^{18} 1.0219; n_α^{18} 1.5307; MR_α 49.03.

$C_{11}H_{14}OF_3$. Calculated: MR_α 49.07.

Kizhner's figures: b.p. 151-152° at 51 mm; b.p. 240-241° at 760 mm; d_0^{20} 1.0316.

Reaction of Methylphenylcyclopropylcarbinol with Sulfuric Acid

1) Action of 25% sulfuric acid. 30 g of the alcohol was heated to boiling for 5 hours with 120 ml of 25% sulfuric acid. The slightly yellowed top layer was removed and combined with an ether extract made from the aqueous solution. The ether solution was washed with water and desiccated with potash. After the ether had been driven off, vacuum distillation of the residue at 16 mm yielded 15 g (47%) of a substance with a b.p. of 99-101°, which slowly decolorized a $KMnO_4$ solution. Considerable tar (10 g) was left in the distilling flask.

2) Action of 50% sulfuric acid. 66 g of the alcohol was heated to boiling

for 20 minutes with 120 ml of 50% sulfuric acid. The top layer and the ether extracts made from the aqueous solution were washed with water and desiccated with K_2CO_3. After the ether had been driven off, vacuum distillation at 14 mm yielded 27 g (40%) of a substance with a b.p. of 99-101°.

Oxidation of the substance with a b.p. of 99-100° at 14 mm. Oxidation of 17 g of the substance consumed 19 g of $KMnO_4$. The neutral product recovered was 10 g of a substance with a b.p. of 99-100° at 14 mm. The substance recovered did not contain a carbonyl grouping, nor did it decolorize a solution of potassium permanganate or a benzene solution of bromine, but it did react with metallic sodium, which indicates that the substance is an alcohol. The solution of the salts produced by oxidation was evaporated over a water bath; this yielded an acid with a m.p. of 119-120°, which sublimed and exhibited no depression when mixed with a known sample of benzoic acid. The aqueous layer left after the benzoic acid had been removed was found to contain oxalic acid as the latter's potassium salt.

0.1790 g substance: 0.0693 g CaO.
0.2139 g substance: 0.0811 g CaO.
Found %: CaO 38.71, 38.33.
$C_2O_4Ca \cdot 2H_2O$. Calculated %: CaO 38.35.

Analysis of the substance with a b.p. of 99-100° at 14 mm:

d_4^0 1.0523; d_4^{18} 0.9997; n_α^{18} 1.5152; MR_α 49.18.

$C_{11}H_{14}OF_3$ (epoxide). Calculated: MR_α 48.55.
$C_{11}H_{14}OF_3\square$ (cyclobutanol). Calculated: MR_α 48.81.

0.2193 g substance: 0.6520 g CO_2; 0.1666 g H_2O.
0.1463 g substance: 0.4426 g CO_2; 0.1152 g H_2O.
Found %: C 81.37, 81.09; H 8.68, 8.50.
$C_{11}H_{14}O$ Calculated %: C 81.48; H 8.63.

0.1892 g substance: 20.93 g benzene: Δt 0.295°.
0.2992 g substance: 24.37 g benzene: Δt 0.375°.
Found: M 162.4, 166.9.
$C_{11}H_{14}O$. Calculated: M 164.

0.0962 g substance: 10.1 ml CH_4 (19°, 760.8 mm).
0.0808 g substance: 7.1 ml CH_4 (19°, 760.8 mm).
0.0821 g substance: 7.2 ml CH_4 (19°, 760.8 mm).
Found: OH 7.2, 6.3, 6.3.
Found%: active H atoms, 0.71, 0.60, 0.60.
Calculated%: OH 10.5, active H atoms, 1.0.

The reaction of the synthesized alcohol with methyl-magnesium iodide was carried out on a large scale in solutions of absolute ethyl or absolute amyl ethers.

4.4 g of CH_3I in 5 ml of isoamyl ether was added to 0.74 g of magnesium moistened with 15 ml of isoamyl ether. After all the magnesium had reacted, a solution of 5 g of the substance with a b.p. of 99-100° at 14 mm in 6 ml of isoamyl ether was added. When heated over a water bath the liquid turned cloudy, but no gas was evolved; only when the reaction mixture was heated over a burner was gas evolved abundantly: 800 ml (690 according to theory). After no more gas was evolved, the organomagnesium compound was decomposed, and the reaction products were extracted with ether. After desiccation and the driving off of the ethyl and isoamyl ethers, distillation yielded 3.9 g (76%) of a fraction with a b.p. of 99-101°

*The reaction with methylmagnesium iodide proceeded with difficulty, the mixture had to be warmed.

at 14 mm: methylphenylcyclobutanol.

Oxidation of methylphenylcyclobutanol (b.p. 99-100° at 14 mm) by a chromic acid mixture. 15 g of the alcohol was added drop by drop, with constant stirring, to a chromic acid mixture of theoretical composition (9 g $K_2Cr_2O_7$, 12 g H_2SO_4, and 100 g H_2O). The reaction mixture was heated over a water bath for 2.5 hours, causing the brown solution to turn green. The neutral oxidation products were driven off with steam, extracted with ether, and distilled at 14 mm; this yielded 7.2 g (50%) of the original product with a b.p. of 99-101° plus acetophenone, the semicarbazone of which exhibited no depression when mixed with a sample of the semicarbazone of known acetophenone.

Oxidation of methylphenylcyclobutanol by nitric acid, by the Demyanov method. 19 g of the alcohol was heated with ten times its weight of nitric acid (sp. gr. 1.40), diluted with 3 volumes of water, in a flask fitted with a reflux condenser over a water bath. Within half an hour a violent reaction set in, and nitrogen oxides were evolved. The flask was chilled, after which heating was continued quietly for one hour and a half. The resulting solution was evaporated over a water bath until all the nitric acid and nitrogen oxides had been eliminated; this caused a considerable quantity of an acid with a m.p. of 102-104° (from benzene) to settle out. This salt was converted into a calcium salt by reacting it with a solution of calcium chloride; the calcium salt was identified as calcium oxalate.

Oxidation by dilute nitric acid. 23 g of the alcohol was heated to 90° for 13 hours over a water bath together with 250 ml of dilute (1:3) HNO_3. A heavy oil collected at the bottom of the flask; it was removed and combined with ether extracts of the aqueous solution. The solution was then neutralized with potash, and the neutral products remaining in solution were driven off with steam and extracted with ether. After the ether had been driven off, distillation at 14 mm yielded 10.5 g of a substance with a b.p. of 99-102°. The aqueous distillate of the neutral products and a small quantity of the low-boiling fraction recovered in fractionation were tested for carbonyl groupings. No carbonyl groupings were found. Hence, the neutral products consisted entirely of the unreacted original alcohol (50%).

Analysis of the solution of the acid salts produced by oxidation yielded 5.3 g of an acid with a m.p. of 119-120°. This acid sublimed and exhibited no depression when mixed with a sample of known benzoic acid. No oxalic acid was found in the reaction products.

Oxidation of methylphenylcyclobutanol by heating with a solution of potassium permanganate. 6.5 g of $KMnO_4$ and 150 ml of water were added to 10 g of the alcohol. The resultant mixture was heated, with constant stirring over a water bath at 50°. As the solution in the flask lost color, finely powdered $KMnO_4$ was added. Oxidation was continued for 6 hours, 13 g of $KMnO_4$ being used. The deposited MnO_2 was filtered out, and the neutral products were extracted from it by heating with ether. The filtrate was steam distilled to eliminate the neutral products, which were extracted from the distillate with ether. The ether extracts were combined and desiccated with calcined potash. After the ether had been driven off, we recovered 3.5 g of a fraction with a b.p. of 90-92° at 9 mm, which agrees with the original alcohol, which has a m.p. of 99-101° at 14 mm. The salt solution was evaporated over a water bath and then acidulated with dilute sulfuric acid. No carbon dioxide was evolved when this was done, but a voluminous precipitate of an acid settled out, weighing 5.8 g. The melting point of the acid was 78-79°. The same acid, with a m.p. of 78-79°, was extracted by ether from the aqueous solution.

The crystalline acid turned into a syrupy liquid after standing for a week over calcium chloride in an exsiccator. No oxalic acid was found in the oxidation products.

Reoxidation of the 3.5 g of alcohol again yielded the crystalline acid (1.5 g) with a m.p. of 78-79°. This time the acid was placed in an exsiccator together with sulfuric acid, but it turned into a liquid after only 18 hours. In a third oxidation, the acid was immediately recovered as a liquid. Inasmuch as oxidation of methylphenylcyclobutanol might also yield dimethyphenylacetic acid, which has the same melting point of 78-80°, we synthesized dimethylphenylacetic acid in order to identify the acid we had produced.

Synthesis of dimethylpherylacetic acid. 20 g of amygdalic acid was heated for 6 hours over a water bath together with 150 ml of absolute methanol and 7 ml of concentrated sulfuric acid. The excess methanol was driven off, and the liquid residue was neutralized with soda, diluted with water, and extracted with ether. After having been desiccated with calcined sodium sulfate, the ether was driven off, and the remaining methyl amygdalate was distilled in vacuum, its crystals separating out in the condenser. The resulting 13 g of the ester served as one of the components for synthesizing the glycol by a Grignard reaction. A solution of 13 g of methyl amygdalate in absolute ether was added in the course of 3 hours to a solution of methylmagnesium iodide in absolute ether, prepared from 8 g of Mg and 13 g of CH_3I. The organomagnesium compound was decomposed, and the resulting glycol was extracted with ether.

After the ether had been driven off, the residual liquidwas heated for two hours over a water bath with 4 g of potassium hydroxide dissolved in 40 ml of alcohol. After heating was complete, the alcohol was driven off, and the glycol was extracted with ether and (after the ether had been driven off) distilled in vacuum. The resultant 4.6 g of the glycol was placed in a Wurtz flask together with 30 ml of dilute (1:5) sulfuric acid and distilled with steam. Ether extracts were made of the distillate, and the residue left after the ether had been driven off was distilled at 8 mm; this yielded 2.5 g of dimethylphenylacetaldehyde, with a b.p. of 87-90°. 2.5 g of the aldehyde was heated for 6 hours with twice the quantity of silver oxide required by theory. The deposit was filtered out of the solution, which was neutralized with soda, condensed over a water bath, and acidulated with (1:5) sulfuric acid. This caused a precipitate of dimethylphenylacetic acid, with a m.p. of 78-79°, to settle out.

Analysis of the silver salt:

0.1135 g substance: 0.0453 g Ag.
Found %: Ag 39.91.
$C_{10}H_{11}O_2Ag$. Calculated %: Ag 39.84.

This acid remained crystalline after being kept for a long time exposed to the air. A test sample mixed with the synthesized acid that had a m.p. of 78-79° exhibited a marked depression of the melting point.

A subsequent endeavor to produce the crystalline acid by oxidizing the alcohol again yielded the acid as a liquid. Extracting it with ether and driving off the ether, we obtained it in crystalline form and analyzed it that same day.

0.1014 g substance: 0.2671 g CO_2; 0.0652 g H_2O.
0.0820 g substance: 0.2188 g CO_2; 0.0542 g H_2O.
Found %: C 72.56, 72.77; H 7.19, 7.40.
$C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31.

Analysis of the syrupy acid.

0.0917 g substance: 0.2760 g CO_2; 0.0566 g H_2O.
0.1716 g substance: 0.4640 g CO_2; 0.1050 g H_2O.
Found %: C 73.16, 73.73; H 6.90, 6.84.
$C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31.

0.1113 g substance: 20.72 g acetic acid: Δt 0.130°.
0.1222 g substance: 20.84 g acetic acid: Δt 0.145°.
Found %: M 161, 157.
$C_{10}H_{12}O_2$. Calculated %: M 164.

The acid was dissolved by heating it in 25% ammonia over a water bath. The excess ammonia was eliminated by heating, and then the salt was precipitated by a concentrated solution of $AgNO_3$. The salt deposit was washed with water and alcohol and then dried.

0.1632 g substance: 0.0605 g Ag.
0.0567 g substance: 0.0239 g Ag.
Found %: Ag 37.07, 36.96.
$C_{10}H_{11}O_2Ag$. Calculated %: Ag 39.84.
$C_{10}H_{11}O_2Ag \cdot H_2O$. Calculated %: Ag 37.34.

Reaction of Methylphenylcyclopropylcarbinol with Hydrochloric Acid

1) 30 g of the alcohol was poured into 68 ml of dilute (1:1) hydrochloric acid in the course of 15 minutes, with constant stirring and chilling with ice. Stirring lasted 3 hours, after which the solution was extracted with ether. After the ether had been driven off, the product was distilled in vacuum; it proved to be the unreacted methylphenylcyclopropylcarbinol. Hence, the action of dilute hydrochloric acid does not result in formation of a chlorohydrin of methylphenylcyclopropyl-carbinol, the alcohol being recovered unchanged.

2) 95 g of the alcohol was poured into 108 ml of hydrochloric acid (sp.gr. 1.19) in the course of 20 minutes, with stirring and chilling. The stirring and chilling of the resulting mixture were continued for 3 hours. The top layer was removed and washed with water. Ether extracts were made of the acid layer diluted with water, and then combined with the top layer. The combined extracts were desiccated with calcium chloride. After the ether had been driven off, the product was distilled at 14 mm, the following fractions being collected:

1) 96-100° 10.5 g
2) 100-125° 5.5 g
3) 125-134° 8.5 g
4) 134-136° 63.5 g (66.8%)
5) A viscous residue that changed into a hyaline mass.

The fraction with a b.p. of 134-136° at 14 mm decolorizes a potassium permanganate solution and contains a trace of an unsaturated chloride. We failed in our efforts to separate the cyclic and unsaturated chlorides by means of repeated fractionation. Repeated fractionation enabled us to collect the fraction with a b.p. of 96-100° at 14 mm over a 94-97° range.

Analysis of the fraction with a b.p. of 94-97° at 14 mm.

d_4^0 0.9710; d_4^{18} 0.9520; n_α^{18} 1.5425; MR_α 47.52.
$C_{11}H_{12}F_6$. Calculated: MR_α 48.08.

0.1477 g substance: 22.05 g benzene: Δt 0.240°
0.1282 g substance: 23.35 g benzene: Δt 0.195°
Found: M 142.3, 143.6.
$C_{11}H_{12}$. Calculated: M 144.

Oxidation of the $C_{11}H_{12}$ hydrocarbon. 4 g of the hydrocarbon was oxidized in the cold with a saturated solution of potassium permanganate. 9 g of the oxidant was used. The manganese dioxide was filtered out, and the filtrate was distilled with steam. The distillate was extracted with ether, and the extracts were dried with calcium chloride. After the ether had been driven off, distillation in vacuum yielded 2 g of a substance with a b.p. of 93-95° at 14 mm. The salt solution was extracted with ether after it had been evaporated over a water bath and acidulated. After the ether had been driven off, the acid that remained in the distillation flask crystallized. After double sublimation the acid fused at 121° and exhibited no depression when mixed with a test sample of known benzoic acid. The SO_4'' ion was eliminated from the aqueous solution remaining after the benzoic acid had been extracted, and the oxalic acid was precipitated with a hot solution of calcium chloride. The precipitate of the salt was dried in an exsiccator and then analyzed.

0.1342 g substance: 0.0516 g CaO.
Found %: CaO 38.45.
$C_2O_4Ca \cdot 2H_2O$. Calculated %: CaO 38.35.

Oxidation of the substance with a b.p. of 134-136° at 14 mm. In order to eliminate the unsaturated impurity, 63.5 g of the chloride with a b.p. of 134-135° at 14 mm was oxidized in the cold by a solution of potassium permanganate. The precipitated MnO_2 was filtered out, washed, and heated with ether in a flask fitted with a reflux condenser in order to extract the neutral products. The latter were also extracted from the distillate recovered when the filtrate was distilled with steam. The ether extracts were combined and dried. After the ether had been driven off, distillation at 9 mm yielded the following fractions:

1) 96-115° 6 g
2) 115-125° 4 g
3) 125-127° 32.5 g.

Fraction 1 consisted of acetophenone, which was identified as its semicarbazone, which exhibited no depression when mixed with a test sample of the semicarbazone of known acetophenone. Fraction 3 did not decolorize a solution of potassium permanganate; it was a cyclic chloride. The acid reaction products were obtained by evaporating the salt solution, acidulating it, and then extracting it with ether. Driving off the ether yielded a crystalline acid that fused at 87-88° after recrystallization from benzene. Calcium oxalate was precipitated from the aqueous solution remaining after the foregoing acid had been extracted.

0.2474 g substance: 0.0952 g CaO.
0.1154 g substance: 0.0444 g CaO.
Found %: CaO 38.52, 38.48.
$C_2O_4Ca \cdot 2H_2O$. Calculated %: CaO 38.35.

Analysis of the Acid with a m.p. of 87-88°

0.1038 g substance: 0.2324 g CO_2; 0.0584 g H_2O.
0.1036 g substance: 0.2317 g CO_2; 0.0597 g H_2O.
Found %: C 61.06, 60.99; H 6.31, 6.44.
$C_{10}H_{12}O_4$. Calculated %: C 61.22; H 6.12.

Analysis of the cyclic chloride with a b.p. of 125-127° at 9 mm:

d_4^0 1.0631; d_4^{18} 1.0483; d_4^{20} 1.0392; n_α^{18} 1.5296; MR_α 53.13.

$C_{11}H_{13}ClF_3O$. Calculated MR_α 52.13.

0.1887 g substance: 20.35 g benzene: Δt 0.270°.
Found: M 182.0.
$C_{11}H_{13}Cl$. Calculated: M 180.5

0.1085 g substance: 0.0841 g AgCl.
0.2147 g substance: 0.1693 g AgCl.
Found %: Cl 19.23, 19.47.
$C_{11}H_{13}Cl$. Calculated %: Cl 19.66.

Oxidation of the chloride with a b.p. of 125-127° at 9 mm. 1) 30 g of the chloride was heated with a saturated solution of potassium permanganate over a boiling water bath in a flask fitted with a stirrer and a reflux condenser. As the solution lost color, finely powdered $KMnO_4$ was added. Oxidation was too thoroughgoing under these conditions, traces of a ketone and an acid (benzoic) being recovered.

2) 22 g of the chloride was placed in a 1-liter flask fitted with a stirrer and containing 0.5 liter of a 1% solution of potassium permanganate. The reaction was carried out by heating the mixture over a water bath; the bath temperature was kept at 45-55° (at 40° the reaction was extremely slow). As the solution lost color, finely powdered $KMnO_4$ was added in small batches. When 64 g of $KMnO_4$ had been used up, the decolorization of the solution was stopped. The deposited MnO_2 was filtered out, washed with hot water, and heated with ether over a water bath. The aqueous solutions were distilled with steam, and the neutral products were extracted from the distillate with ether. Driving off the ether yielded a certain amount of the unoxidized chloride.

The salt solution was evaporated and acidulated with sulfuric acid, which caused a precipitate to settle out; sublimation of this precipitate yielded an acid with a m.p. of 120°, which proved to be benzoic acid. Ether extracts were made of the filtrate left after the benzoic acid had been filtered out. Driving off the ether yielded a crystalline acid with a m.p. of 71-74°, the m.p. of which was 85-86° after double recrystallization. A sample mixed with the acid produced by oxidizing the unsaturated chloride exhibited no depression.

Determination of active hydrogen by the Terentyev-Shcherbakov method, in a CO_2 atmosphere:

0.0706 g substance: 23.7 ml CH_4 (13.7°, 758 mm).
0.0461 g substance: 18.9 ml CH_4 (13.7°, 758 mm).
Found %: active hydrogen 1.40, 1.71;
Found %: active H atoms, 2.72, 3.30.
$C_{10}H_9O(OH)_3$. Calculated %: active hydrogen, 1.63; active H atoms 3.0.

Oxidation of the $C_{10}H_{12}O_4$ acid. 0.7 g of the acid was heated with 7 ml of dilute (1:3) nitric acid for 2 hours over a boiling water bath. After cooling, a deposit of a crystalline acid (0.5 g) settled out; this fused at 119.5-120° after sublimation and proved to be benzoic acid. The filtrate was neutralized with soda, heated to boiling, and precipitated with a solution of $CaCl_2$. A precipitate of calcium oxalate was thrown down.

Saponification of the cyclic chloride with a b.p. of 125-127° at 9 mm.

1) 10 g of the chloride was heated to boiling for 150 hours with a 20% solution of potash. The top layer was removed, and ether extracts were made of the aqueous layer. Driving off the ether yielded 7 g of the chloride with a b.p. of 125-127° at 9 mm.

2) 49 g of the chloride was heated in a flask for 144 hours with 170 ml of a 15% solution of NaOH. The top layer was removed, desiccated with $CaCl_2$, and distilled in vacuum at 9 mm. 31 g of a fraction with a b.p. of 125-127° was collected.

Initial chloride: b.p. 125-127° at 9 mm; d_4^{18} 1.0488.
Chloride after saponification: b.p. 125-127° at 9 mm; d_4^{18} 1.0482.

Reaction of a mixture of the unsaturated and cyclic chlorides with an alcoholic solution of NaOH. 22 g of the mixture of the unsaturated and cyclic chlorides produced by the action of concentrated hydrochloric acid upon methylphenylcyclopropylcarbinol was heated for 14 hours with a 10% alcoholic solution of NaOH. The alcohol was driven off, extracted with ether, and desiccated with K_2CO_3. The following fractions were collected after repeated fractionation at 16 mm:

1	96-199°	10 g,
2	99-117°	3 g,
3	117-118°	3.5 g.

None of the fractions contained a halogen or reacted with metallic sodium; they all decolorized a solution of potassium permanganate. It was noticed that all these fractions thicken in storage; within a week Fractions 2 and 3 turned into thick, viscous masses; the former was slightly more mobile. Redistillation of this fraction yielded the same polymer in the residue, while the distillate consisted of 4 g of a substance with a b.p. of 96-99°, which reacted energetically with maleic anhydride, and, hence, was a1-3-diene hydrocarbon, the product of detaching hydrogen chloride. The structure of the hydrocarbon was borne out by it oxidation. 3 g of the hydrocarbon was oxidized in the cold with a solution of $KMnO_4$. The precipitate of MnO_2 was filtered out, and the filtrate was distilled with steam and extracted with ether. Driving off the ether yielded 1.7 g of a substance with the odor of acetophenone, which distilled at 95-98° and 14 mm. This substance yielded a precipitate of the semicarbazone of acetophenone.* The thicker fraction resulting from saponification, which boils at 117-118° and 10 mm, is a mixture of the monomer and the dimer of the hydrocarbon as is indicated by the determination of its molecular weight:

0.1099 g substance: 16.35 g benzene: Δt 0.160°
0.2076 g substance: 16.35 g benzene: Δt 0.325°
Found: M 214, 210.
$C_{11}H_{12}$. Calculated: M 144.
$(C_{11}H_{12})_2$. Calculated: M 288.

SUMMARY

1. A study has been made of the action of sulfuric and hydrochloric acids upon methylphenylcyclopropylcarbinol.

2. It has been found that the action of sulfuric acid upon methylphenylcyclopropylcarbinol expands the ring, giving rise to 1,1-methylphenylcyclobutanol-2, and dehydrates the initial alcohol, giving rise to 2-phenylpentadiene-1,4.

3. When hydrochloric acid acts upon methylphenylcyclopropylcarbinol, the

*It exhibited no depression when mixed with a test sample of the semicarbazone of known acetophenone.

formation of chlorides is accompanied by an isomeric transformation, along two lines: 1) the rupture of the three-membered ring and the formation of an unsaturated primary chloride, 2-phenyl-5-chloropentene-2; and 2) the expansion of the three-membered ring to a four-membered one and a migration of the chlorine atom along the ring.

4. The unsaturated primary chloride is not cyclized by alkaline reagents, but liberates hydrogen chloride and gives rise to a 1,3-diene hydrocarbon.

5. The chlorohydrin of 1,1-methylphenylcyclobutanol is unaffected by aqueous solutions of alkalies, but when reacted with an alcoholic solution of an alkali, it suffers rupture of its four-membered ring, accompanied by the detaching of hydrogen chloride and the formation of a 1,3-diene hydrocarbon.

LITERATURE CITED

[1] T.A.Favorskaya and S.A.Friedman, J.Gen. Chem., 15, 421, (1945).

[2] T.A.Favorskaya, J.Gen. Chem., 17, 541 (1947).

[3] T.A.Favorskaya and S.A.Friedman, J. Gen. Chem., 18, 2080 (1948).

[4] N.M.Kizhner, J. Russ. Chem. Soc., 43, 1163 (1911).

[5] N.D.Zelinsky, Ber., 34, 3887 (1901).

[6] N.M.Kizhner, J. Russ. Chem. Soc., 42, 1211 (1910).

[7] N.Ya.Demyanov, J. Russ. Chem. Soc., 43, 835 (1911).

[8] T.A.Favorskaya and S.A.Friedman, J. Gen. Chem., 18, 2085 (1948).

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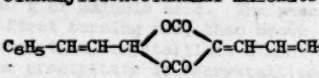
RESEARCH ON THE β-LACTONES AND β-LACTONIC ACIDS

VIII. CONDENSATION OF CINNAMALDEHYDE WITH MALONIC ACID

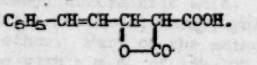
N. S. Vulfson

Condensations of cinnamaldehyde with malonic acid in the presence of the principal catalysts, which result in the formation of cinnamylidenemalonic and cinnamylideneacetic acids, have been frequently described in the literature [1-8].

Michael and Weiner [9] tried to condense cinnamaldehyde with malonic acid in Ott [10] and Meldrum [11] reactions. In the first reaction they were able to recover nothing but cinnamylidinemalonic acid, while in the second they secured, in addition to this acid, a new product, yellow in color and with a m.p. of 157°, which decomposes to cinnamylidenemalonic acid when heated with an alkali , and yields the phenylhydrazide of cinnamaldehyde when heated with phenylhydrazine. They assigned it the structure of cinnamylidenecinnamal malonate:



Continuing my research on the β-lactones and β-lactonic acids, I felt I had to spend more time on this condensation and repeat the work done by the earlier authors, especially as the theoretical considerations set forth in my preceding report [12] indicate that this reaction, too, ought to yield a β-lactonic acid, the β-lactone of cinnamylidenemalonic acid:



When I repeated the condensation of cinnamaldehyde with the "Ott reagent" (see Report V [14]), I was able to show that cinnamylidenemalonic acid is not the sole product, cinnamylidenecinnamal malonate, with a m.p. of 154.5-155.5°, which is identical with that produced in the Meldrum reaction, also being formed, and that the cinnamylidenemalonic acid gives rise to cinnamaldehyde as well.

In my analysis of these compounds I noted its curious property of titrating in the cold like a monobasic acid, and of being regenerated unchanged when acidified. A special experiment made with cinnamaldehyde diacetate has demonstrated that such partial saponification with an alkali in the cold is a general property of such ortho

esters of cinnamaldehyde.

The formation of cinnamylidenecinnamal malonate under these circumstances must be attributed to the considerably greater tendency of cinnamaldehyde to form ortho esters, especially in the presence of concentrated sulfuric acid, which catalyzes this process, according to Wagscheider and Spath [13]. The reasons for the formation of cinnamylidenemalonic acid will be discussed below.

When cinnamaldehyde is condensed under milder conditions, i.e, with a "primary mixed anhydride" [14] or when acetyl chloride is reacted with neutral silver malonate in the presence of the aldehyde, we secure, in addition to cinnamylidenemalonic acid, the sought-for β-lactonic acid: a lactone of cinnamylidenemalonic acid in the form of a white crystalline substance that fuses with decomposition at 132-133° (a test sample mixed with malonic acid exhibits a marked depression). When the β-lactonic acid is boiled for 2 hours in an acetone solution, much of it undergoes a tautomeric change to cinnamylidenemalonic acid. This thermolability explains the preponderant formation of cinnamylidenemalonic acid when cinnamaldehyde is condensed with the "Ott reagent", which is accompanied by the evolution of considerable heat. The cinnamylidenemalonic acid that is formed condenses in turn with another molecule of cinnamaldehyde, giving rise to an ortho ester - cinnamylidenecinnamal malonate.

Thus, notwithstanding the somewhat unusual nature of the reaction involving the condensation of cinnamaldehyde, it fully corroborates the theoretical assumptions expressed in the preceding report [12].

In conclusion, I consider it my duty to express my profound gratitude to Academician V.M.Rodionov and Prof. M.M.Shemyakin for their valued counsel and suggestions.

EXPERIMENTAL

1. Ott condensation. 12.2 g of cinnamaldehyde is poured into an "Ott reagent," prepared with 10 g of malonic acid. The reaction mixture evolves very much heat and changes color, first turning red, then brown, green, and, finally, black. The mass, left to stand overnight, crystallizes almost completely and is then decanted with chloroform. The precipitate is recrystallized from an acetone-chloroform mixture. This yields 6 g of a white crystalline substance with a m.p. of 133-134°, which exhibits no depression when mixed in a test sample with malonic acid. The chloroform solution is evaporated. The crystals that settle out upon cooling are filtered out and twice recrystallized from 70% alcohol. This yields 3 g of yellow, acicular crystals with a m.p. of 205-206°, which exhibit no depression when mixed in a test sample with cinnamylidenemalonic acid. The chloroform mother liquor is evaporated to dryness, and the residual, tarry, yellow-orange mass is repeatedly extracted with petroleum ether. Part of the solvent is driven off. Upon cooling a bright yellow substance with a m.p. of 154-155.5° (from a benzene-petroleum ether mixture) crystallizes out. Yield: 3 g. A test sample mixed with cinnamylidenecinnamal malonate (see Experiments 2 and 3) exhibits no depression.

2. Meldrum condensation. Three drops of concentrated sulfuric acid are added, with stirring, to 10.4 g of malonic acid, 25 g of acetic anhydride, and 14 g of cinnamaldehyde. The malonic acid dissolves, and the reaction mass turns color, first red, then purple, lilac-colored, and finally, green. It is then left to stand overnight. The precipitate is filtered out and recrystallized from a mixture of benzene and petroleum ether. This yields 7.5 g of cinnamylidenecinnamal malonate as a bright-yellow crystalline substance with a melting point of 155.3-155.7°. Some

cinnamylidenemalonic acid, with a m.p. of 206-207°, is recovered from the filtrate.

Analysis of Cinnamylidenecinnamal Malonate

Found %: C 75.85; H 4.60.
$C_{21}H_{16}O_4$. Calculated %: C 75.90; H 4.82.

Titration of Cinnamylidenecinnamal Malonate

0.0760 g substance:	0.1N NaOH consumed in the cold	2.3 ml.
	Consumed after boiling for half an hour with an excess of alkali	4.5 ml.
$C_{21}H_{16}O_4$:	Computed for a monobasic acid	2.26 ml.
	Computed for a dibasic acid	4.52 ml.

If the solution titrated in the cold is acidified and then extracted with benzene, a bright-yellow crystalline substance with a m.p. of 154-155° is left behind when the benzene is driven off; it exhibits no depression when mixed in a test sample with the initial cinnamylidenecinnamal malonate.

If the solution that is titrated after having been boiled with an excess of alkali and then extracted with ether is acidified, driving off the ether and recrystallizing from 70% alcohol yields a yellow crystalline substance with a m.p. of 204-205°, which exhibits no depression when mixed in a test sample with cinnamylidenemalonic acid.

3. Synthesis of cinnamylidenecinnamal malonate. One drop of concentrated sulfuric acid is added to a mixture of 0.6 g of cinnamylidenemalonic acid, 0.6 g of cinnamaldehyde, 2 g of glacial acetic acid, and 2 g of acetic anhydride, and the whole is set aside to stand overnight. The precipitate is decanted with ether and recrystallized from a mixture of benzene and petroleum ether. This yields 0.7 g of cinnamylidenecinnamal malonate as a bright-yellow crystalline substance with a m.p. of 156.5-157.5°.

Titration

0.0238 g substance:	0.1N NaOH consumed in the cold	0.75 ml
	Consumed after boiling for half an hour with an excess of alkali	1.48 ml
$C_{21}H_{16}O_4$.	Computed for a monobasic acid	0.71 ml
	Computed for a dibasic acid	1.43 ml.

4. Synthesis of the β-lactone of cinnamylidenemalonic acid. 0.6 g of neutral silver malonate is mixed with 2.7 g of cinnamaldehyde, and 5 g of acetyl chloride is carefully added drop by drop. The precipitate of silver chloride is filtered out, and the filtrate is left to stand overnight. The crystals that settle out are decanted with benzene and recrystallized from acetone. This yields 1.4 g of the β-lactone of cinnamylidenemalonic acid as a white crystalline substance that fuses with decomposition at 132-133° (a test sample mixed with malonic acid fuses at 115-124°).

Titration

0.0417 g substance:	0.1N NaOH consumed in the cold	2.00 ml.
	Consumed after boiling ¼ hr. with excess alkali	4.00 ml.
$C_{21}H_{10}O_4$:	Computed for neutralization	1.91 ml.
	Computed for neutralization and saponification	3.82 ml.

Acidification does not yield the original lactonic acid. The analysis of the silver salt produced by silver-nitrate precipitation of a solution of the lactonic acid neutralized with alkali in the cold is as follows:

Found %: Ag 33.42.
$C_{12}H_9O_4Ag$ Computed %: Ag 33.23.

The analysis of the silver salt produced by silver-nitrate precipitation of a solution of the lactonic acid and neutralized with acid after boiling:

Found %: Ag 50.15.
$C_{12}H_9O_4Ag_2$. Computed %: Ag 50.00.

Analysis of the lactonic acid:

Found %: C 65.80; H 4.40.
$C_{12}H_{10}O_4$. Computed %: C 66.05; H 4.58.

After the benzene mother liquor had been washed with water and the solvent had been eliminated, we obtained 0.5 g of a yellow crystalline substance with a m.p. of 205-206° (from 70% alcohol), which exhibited no depression when mixed in a test sample of cinnamylidenemalonic acid.

The reaction of cinnamaldehyde with the "primary mixed anhydride" [14] is similar.

5. Thermal decomposition of the β-lactone of cinnamylidenemalonic acid. 0.2 g of the β-lactonic acid is dissolved in 10 ml of acetone and then boiled for 2 hours with a reflux condenser. The solution gradually turns yellow. Driving off the acetone yields a yellow precipitate with a m.p. of 95-110°. Triple fractional crystallization from methanol yields: a) white crystals with a m.p. of 123-124.5° (exhibiting no depression in a test sample mixed with the original lactonic acid); and b) yellow acicular crystals with a m.p. of 202-204° that exhibit no depression when mixed in a test sample with cinnamylidenemalonic acid.

6. Synthesis of cinnamaldehyde diacetate. The cinnamaldehyde diacetate was prepared by the Wegscheider method [13]: from 10 g of the aldehyde and 20 g of acetic anhydride with 1 drop of concentrated sulfuric acid present. The yield was 11.5 g of white acicular crystals with a m.p. of 84-85°. It decomposes when stored.

Titration

0.2096 g substance:	0.1N NaOH consumed in the cold	9.0 ml.
	Consumed after boiling ½ hr. with excess alkali	18.1 ml.
$C_{13}H_{14}O_4$.	Computed for a monobasic acid	8.95 ml.
	Computed for a dibasic acid	17.91 ml.

SUMMARY

1. When cinnamaldehyde is condensed with malonic acid in an Ott reaction, cinnamylidenemalonic acid is not the sole reaction product, cinnamylidenecinnamal malonate also being formed.

2. When the reaction is carried out under milder conditions, we get the β-lactone of cinnamylidenemalonic acid, in addition to the acid itself. The properties of the β-lactone conform to those of all the β-lactones of this type synthesized hitherto.

3. When an acetone solution of the β-lactone of cinnamylidenemalonic acid is heated, it is changed tautomerically into cinnamylidenemalonic acid.

4. When cinnamylidenecinnamal malonate is reacted in the cold with an alkali solution, it titrates as a monobasic acid and is regenerated by acidification. When this compound is boiled with an excess of an alkali solution, it titrates as a dibasic acid and yields cinnamylidenemalonic acid when acidified.

LITERATURE CITED

[1] Dutt, J. Indian Chem. Soc., 1, 297 (1924-1925).

[2] Dalal, Dutt, J. Indian.Chem. Soc., 9, 309 (1932).

[3] Kurien, Pandia, Surange, J. Indian Chem. Soc., 11, 823 (1934).

[4] Knoevenagel, Ber., 31, 2596 (1898).

[5] Doebner, Ber., 35, 2129 (1902).

[6] Knoevenagel, German patent 97735.

[7] Knoevenagel, German patent 164296.

[8] Riedel, Lieb. Ann., 361, 96 (1908).

[9] Michael, Weiner, J. Am.Chem.Soc., 58, 680 (1936).

[10] Ott, Lieb. Ann., 401, 159 (1913).

[11] Meldrum, J.Chem.Soc, 93, 598 (1908).

[12] N.S.Vulfson, Report VII, J.Gen.Chem., 20, No. 3, (1950).*

[13] Wegscheider, Spath, Monatsh., 30, 825 (1909).

[14] N.S.Vulfson, Report V, J.Gen.Chem. 19, 1904 (1949).**

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*See CB translation p. 449 ff.

**See CB translation p. a-369 ff.

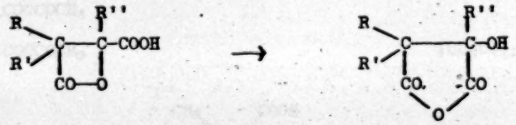
RESEARCH ON THE β-LACTONES AND β-LACTONIC ACIDS

IX. DECARBOXYLATION OF β-LACTONIC ACIDS

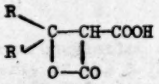
N. S. Vulfson

The decarboxylation of the β-lactones, resulting in the formation of olefins, has been investigated very thoroughly [1-7].

The β-lactonic acids that are derivatives of malic acid are isomerized by heating to anhydrides of dicarboxylic acids [8,9]:



The β-lactonic acids that are derivatives of malonic acid:



behave quite differently.

Ott [10] heated the β-lactone of isopropylidenemalonic acid and described a "ketonic-type" cleavage, 80% of the theoretical quantities of acetone and carbon suboxide being recovered. He was unable to find a decarboxylation product – dimethylacrylic acid. The α-bromine and α-methyl derivatives of this lactonic acid behave similarly, giving rise to the methylbromoketene and dimethylketene, respectively, though the lactone ring is much more stable in these compounds than in the β-lactone of isopropylidenemalonic acid.

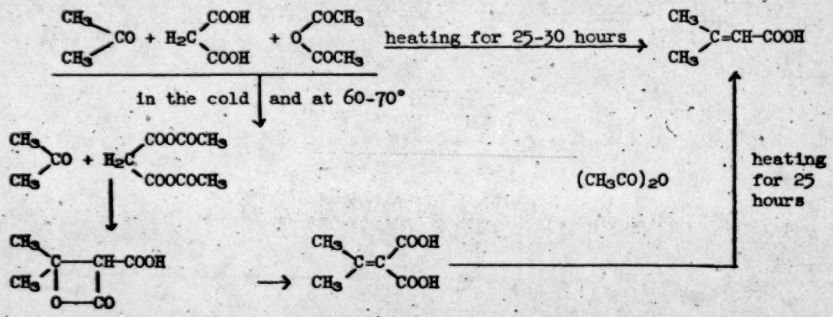
When the Ott [10,11] method of synthesizing the β-lactone of isopropylidenemalonic acid by condensing a mixed malonic-acetic anhydride with acetone in the presence of concentrated sulfuric acid is compared with the Massot method [12] of synthesizing dimethylacrylic acid by the prolonged heating of acetone with malonic acid in acetic anhydride, we are struck by their close similarity. This resemblance becomes even greater in the synthesis of β-lactonic acids by my modification of Ott's method, with no concentrated sulfuric acid present (with the so-called "primary mixed anhydride") [12].

This resemblance led me to conjecture that the β-lactone of isopropylidenemalonic acid is an intermediate product in the Massot synthesis.

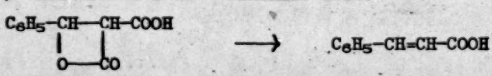
If this hypothesis is correct, the decarboxylation of the β-lactonic acid should result in formation of dimethylacrylic acid. All efforts to produce decarboxylation by simple heating, or by heating to above 100° in vacuum, in a pyridine solution or in acetic anhydride proved fruitless, which agrees fully with Ott's observation; but heating for 25 hours to 60-70° in acetic anhydride yielded a small quantity of dimethylacrylic acid. Isopropylidenemalonic acid undergoes decarboxylation under the same conditions.

This type of decarboxylation of the β-lactone of isopropylidenemalonic acid fully conforms with the general type of decarboxylation of β-lactones described in the literature [1-7].

Thus, the mechanism of the Massot reaction for the synthesis of dimethylacrylic acid may be represented as follows:



To test whether this decarboxylation applies to all β-lactonic acids of this type or is a particular property of the β-lactone of isopropylidenemalonic acid, a similar reaction (heating to 60-70° with acetic anhydride for 20-25 hours) was carried out with the β-lactone of benzylmalonic acid. This also yielded the corresponding α, β-unsaturated acid – cinnamic acid.



This line of reasoning is likewise borne out by the observation that the β-lactone of cinnamylidenemalonic acid is changed tautomerically into cinnamylidenemalonic acid when heated in an acetone solution [13].

In conclusion, the author wishes to express his profound indebtedness to Academician V.M.Rodionov and Prof. M.M.Shemyakin for their valued, numerous suggestions and advice.

EXPERIMENTAL

1. Decarboxylation of the β-lactone of isopropylidenemalonic acid. 1 g of the β-lactonic acid was heated to 60-70° with 10 ml of acetic anhydride for 25 hours over a water bath. The solvent was driven off and the residue was distilled at 20 mm

residual pressure, with partial decomposition. This yielded 0.3 g of a light-yellow oily liquid, which slowly crystallized completely into elongated needles.

M.p.: 64-66° after recrystallization from water. A test sample mixed with dimethylacrylic acid exhibits no depression.

Titration

0.0502 g substance: 0.1N NaOH consumed 5.14 ml
$C_5H_8O_2$. Computed for neutralization, 5.04 ml.

2. Decarboxylation of isopropylidenemalonic acid. 1.5 g of isopropylidenemalonic acid and 20 g of acetic anhydride were heated over a water bath to 60-70° for 25 hours. Subsequent treatment was the same as that described above. This yielded 0.2 g of dimethylacrylic acid with a m.p. of 66-68°, which exhibited no depression when mixed with an analytical sample.

Titration

0.0936 g substance: 0.1N NaOH consumed 9.40 ml
$C_5H_8O_2$. Computed for neutralization 9.36 ml.

3. Decarboxylation of the β-lactone of benzylmalonic acid. 3.5 g of the lactonic acid was dissolved in 35 ml of acetic anhydride and then heated over a water bath to 60-70° for 20-26 hours. Then the acetic anhydride was driven off in vacuum, and the residue was recrystallized from methanol. This yielded 1.5 g of cinnamic acid with a m.p. of 131-132°. A test sample mixed with an analytical sample exhibited no depression.

Titration

0.1364 g substance: 0.1N NaOH consumed 9.28 ml.
$C_9H_8O_2$. Computed for neutralization 9.21 ml.

SUMMARY

When the β-lactonic acids that are derivatives of malonic acid are heated to 60-70° for a long time in an acetic-anhydride solution, they are decarboxylated, giving rise to α,β-unsaturated acids of the type that is common to all β-lactones.

LITERATURE CITED

[1] Einhorn, Ber., 16, 2208 (1883).
[2] Basler, Ber., 16, 3001 (1883).
[3] Pransnitz, Ber., 17, 595 (1884).
[4] Einhorn, Hess, Ber., 17, 2015 (1884).
[5] Eihengrun, Einhorn, Ber., 23, 2876 (1890).
[6] Salkowski, J. prak. Chem., 106, 253 (1923).
[7] Staudinger, Ber., 55, 647 (1922).
[8] Fichter, Hissch, Ber., 33, 3270 (1900).
[9] Bains, Thorpe, J. Chem. Soc., 123, 2743 (1923).
[10] Ott, Lieb. Ann., 401, 159 (1913).
[11] N.S.Vulfson, J. Gen. Chem., 19, 1904 (1949).*
[12] Massot, Ber., 27, 1225 (1894).

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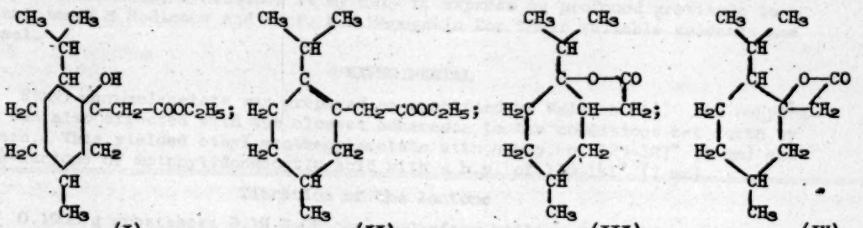
RESEARCH ON THE β-LACTONES AND β-LACTONIC ACID

X THE β-LACTONE OF METHYLIDENEACETIC ACID

N. S. Vulfson

In heating ethyl mentholacetate (I), produced by a Reformatsky condensation of menthone with bromoacetoacetic ester, with potassium bisulfate, Wallach [1] noted that another reaction product was formed, besides the normal dehydration product: the ester of menthenylacetic acid (II). The former product boils at 300-305°, and has a sp.gr. of d^{20} 1.015 and a n_D^{20} of 1.4781. Heating it with hydrogen iodide yields a crystalline modification with a m.p. of 88.5-89.5° (from methanol). It is titrated by boiling with an alkali, being recovered unchanged when acidulated. This led Wallach to assign the structure of a γ-lactone (III) to this compound:



(I) (II) (III) (IV)

Kuhn and Hoffer [2] synthesized the identical lactone by heating one of the chlorolactones recovered from the product of condensing citral with malonic acid, and they therefore ascribed the structure of a γ-lactone to the compound they were examining.

My previous researches [3] made me believe it to be unlikely that the compound (III) contained a γ-lactone ring. The reversibility of the ring-opening process when heated with alkali is far from convincing proof of the existence of a five-membered ring, inasmuch as the reversibility of the ring-rupture of a β-lactone was noted by Bains and Thorpe [4] in the β-lactone of dipropylmalic acid and has

been often illustrated by me in a number of instances. Moreover, there is no structural basis for the formation of a γ-lactone when a β-hydroxy acid is dehydrated.

Synthesizing the lactone described by Wallach and confirming the reversibility of the opening of its ring when acted upon by an alkali, I succeeded in producing a silver salt, the analysis of which indicated that the opening of the lactone ring is tautomeric, with no molecule of water added, resulting in the salt of an unsaturated acid rather than of a hydroxy acid. This fact by itself is not a substantial proof that this is a β-lactone ring, inasmuch as instances are known of similar openings of γ-lactone rings.

Conclusive proof of structure of the lactone could be provided only by study of the products of the oxidation of this compound by potassium permanganate and by its hydrolytic cleavage. If a β-lactone ring is present, oxidation should result in the formation of menthone, whereas if the ring is a γ-lactone, the reaction products should be those of a deeper decomposition of the menthone. Inasmuch as the danger exists that menthone itself may be largely oxidized under the conditions of the experiment, efforts were made to oxidize menthone itself and ethyl mentholacetate (I); they indicated that menthone can be recovered and identified under the given conditions. When we oxidized the lactone (III) with a 0.5% solution of potassium permanganate in the cold, we recovered menthone (identified as its semicarbazone). Menthone was also produced by boiling the lactone (III) with a 50% solution of potassium hydroxide.

These experiments, together with the reversibility and the tautomerism of the opening of the lactone ring prove beyond a doubt that the compound synthesized by Wallach is not a γ-lactone as he had supposed, but the β-lactone of menthylideneacetic acid (IV).

In conclusion, I consider it my duty to express my profound gratitude to Academician V.M.Rodionov and Prof. M.M.Shemyakin for their valuable guidance and counsel.

EXPERIMENTAL

Ethyl mentholacetate was prepared as specified by Wallach [1]. Its dehydration was also effected with the closest adherence to the conditions set forth by Wallach. This yielded ethyl menthenylacetate with a b.p. of 125-127° (7 mm) and the β-lactone of metnhylideneacetic acid with a b.p. of 138-141° (7 mm).

Titration of the lactone

0.1008 g substance: 0.1N NaOH consumed after boiling for half an hour with an excess of alkali ..... 5.06 ml

$C_{12}H_{20}O_2$. Computed for opening the lactone ..... 5.14 m.

After the acid had been neutralized, we recovered drops of an oil with the odor of menthone, which was not titrated by alkali in the cold.

4.57 ml consumed after reboiling for half an hour with an excess of alkali solution.

Acidulation again resulted in the recovery of drops of oil, which was not titrated by alkali in the cold.

Conclusion: the opening of the lactone ring is reversible. The drop in the consumption of alkali when boiling with alkali was repeated is due to partial cleavage by the alkali.

1. Synthesis of the silver salt. 0.5 g of the lactone is boiled for 30 minutes with an excess of alkali solution (containing no soda), the excess of alkali is carefully neutralized with nitric acid (avoiding any excess of the latter), the solution is evaporated in vacuum to a volume of 3-5 ml, and a precipitate is thrown down with silver nitrate.

Found %: Ag 35.36.

$C_{12}H_{19}O_2Ag$. Computed %: Ag 35.64.

2. Oxidation of the β-lactone of menthylideneacetic acid by permanganate. 1 g of the lactone is dissolved in 25 ml of pure acetone, and a 0.5% solution of potassium permanganate is added in 10-15 ml batches. Reduction sets in at once. During the course of 2 hours, 350 ml of permanganate solution is consumed, after which reduction is discontinued. The solution is diluted with a large volume of water and repeatedly extracted with ether. The ether extract is washed with water and dried,, and the ether is driven off. This yields 0.6 g of a light-yellow oil with the odor of menthone. It forms a semicarbazone with a m.p. of 187-188° (from alcohol). A test sample of the semicarbazone mixed with menthone semicarbazone fuses at 187-188°.

3. Oxidation of ethyl mentholacetate by permanganate. 3 g of ethyl mentholacetate is dissolved in 50 ml of pure acetone, and a 0.5% solution of potassium permanganate is added in 10-15 ml batches. In all, 200 ml of permanganate solution is consumed. Subsequent treatment is as indicated above. This yields 1.5 g of an oily substance that forms a semicarbazone with a m.p. of 187.5-188°. A test sample mixed with the semicarbazone of menthone exhibits no depression.

4. The action of potassium permanganate upon menthone. 1 g of menthone is dissolved in 20 ml of pure acetone, and 15 ml of a 0.5% solution of potassium permanganate is added. No noticeable reduction occurs. It is set aside overnight. Reduction is incomplete. Subsequent treatment is as outlined above. This yields 0.7 g of an oily liquid that produces a semicarbazone with a m.p. of 187.5-188°. A test sample mixed with the semicarbazone of menthone exhibits no depression.

5. Hydrolytic cleavage of the β-lactone of menthylideneacetic acid. 1 g of the lactone is boiled with a reflux condenser, over a screen, with 20 ml of a-50% solution of potassium hydroxide. At first everything enters solution, but then oily brown drops with the strong odor of menthone appear. After cooling they are extracted with ether, the ether solution is washed with water and dried, and the ether is driven off. This yields 0.8 g of a light-yellow substance with the odor of menthone. It forms a semicarbazone with a m.p. of 187.3-188.3°. It exhibits no depression when mixed in a test sample with the semicarbazone of menthone.

SUMMARY

The lactone described by Wallach, produced by dehydrating ethyl mentholacetate with potassium bisulfate, contains a β-lactone ring rather than a γ-lactone ring, and hence is the β-lactone of menthylideneacetic acid.

LITERATURE CITED

[1] O. Wallach, Lieb. Ann., 323, 151 (1902); 353, 313 (1907).

[2] R. Kuhn, M.Hoffer, Ber., 64, 1243 (1931).

[3] N.S.Vulfson, VII, J. Gen. Chem., 20, No. 3, (1950).*

[4] L. Bains, J.Thorpe, J. Chem. Soc., 123, 2743 (1923).

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COMMENTS ON THE PAPER BY N. V. VILYAMS AND S. V. VASILYEV

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The paper by N.V.Vilyams and S.V.Vasilyev published in the Journal of General Chemistry (1948, No. 1), deals with a study of the action of N_2O_3 upon petroselinic acid.

Several additions and corrections must be made in this paper. If we start with the problem of the transformation of oleic into elaidic acid, the paper asserts that among Russian authors the only one to deal with this was A.P.Lidov. Yet the well-known paper by A.M.Zaitsev, who proposed SO_2 as an elaidinating agent, was published in 1892 [1]. As for the determination of the position of the double bond in petroselinic acid, this was first done by Vongerichten and Kohler [2], who made use of the Baruch method. Eibner [3] and his co-workers merely corroborated the conclusion reached by Vongerichten and Kohler that petroselinic acid is 6,7-oleic acid: $CH_3(CH_2)_{10}CH{=}CH(CH_2)_4\ COOH$.

More on petroselinic acid: the text states that N.V.Vilyams and S.V.Vasilyev were the first to discover petroselinic acid in oil of coriander. Yet the fatty oil of coriander seed of native origin – from the North Caucasus [4] – was described in rather full detail in the Journal of Applied Chemistry in 1933. In their investigation of oil of coriander, the authors recovered an unsaturated acid with a m.p. of 33-33.5° from the fatty oil of coriander, which was identified as petroselinic acid by its dihydroxy acid, with a m.p. of 119-120°, synthesized by oxidation with potassium permanganate in an alkaline medium by the A.M.Zaitsev method.

At a later date, in 1939, the structure of the unsaturated acid with a m.p. of 33-33.5° isolated from the fatty oil of North Caucasus coriander seed was confirmed by one of these authors by means of ozonation [5]; it turned out to be actually petroselinic acid, inasmuch as lauric and adipic acids were recovered when the ozonide was decomposed. In addition to petroselinic acid, the fatty oil of coriander recovered from the North Caucasus seed was found to contain oleic acid and a small quantity of stearic acid. These authors also expressed the belief that other members of the Umbelliferea family must also contain petroselinic acid, in accordance with the biochemical hypothesis of S.L.Ivanov [6]. Steger and Von Loon have found that the oil of ivy fruit contains 58% of petroselinic acid [7].

Among foreign research workers, Hilditch made a thorough study of British oil of coriander; he and his co-workers also investigated the oil of English parsley [8]. The composition of British and North Caucausus (Starominsk station) oil of coriander is given below.

Composition of the fatty oil of coriander	Source of the oil of coriander	
Acids entering into the composition of the oil of coriander	North Caucausus, Starominsk station	British oil
Palmitic	–	8%
Petroselinic	70 – 75%	53%
Oleic	17 – 20%	32%
Linoleic	–	7%
Higher saturated acids (probably including traces of stearic acid).....	7%	1%

It may be added, in conclusion, that the paper by Vongerichten was published in 1909, and not in 1902.

LITERATURE CITED

[1] A.M.Zaitsev, J. Russ. Phys. Chem. Soc., 24, 477 (1892).

[2] Vongerichten and Kohler, Ber., 42, 1638 (1909).

[3] Eibner, Chem. Umsch., 1927, 312.

[4] J. Appl. Chem., 6, 992 (1933).

[5] A.A.Chernoyarova, J.Gen.Chem., 9, 149, (1939).

[6] S.L.Ivanov. The Science of Vegetable Oils (1924); S.L.Ivanov. The Climates of the Earth, etc..

[7] Steger and J. v.Loon, Chem. Umsch., 1929, 40.

[8] S.P.Hilditch and E.E.Jones, J. Soc. Chem. Ind., 46, 174 (1927).

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THE THEORETICAL PRINCIPLES OF THE CHEMISTRY OF VINYL ETHERS

I OXONIUM PROPERTIES OF VINYL ALKYL ETHERS

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The present paper has as its aim a summary of the theoretical investigations of the conversion of vinyl ethers, a description of the singular nature of these compounds, and a search for the correct ways of exploiting and predicting their properties. Moreover, it is necessary to exclude endeavors to consider the vinyl alkyl ethers as typical derivatives or substitution compounds of ethylene.

The singular properties of vinyl alkyl ethers are due principally to the presence of a double bond immediately adjacent to the atom of oxygen. This combination of a double bond and an oxygen atom is rare and little research has been done upon it. It may be recalled that because of this structure it is wholly impossible for the simplest representative of hydroxy-substituted ethylene – vinyl alcohol – to exist.

The behavior of a molecule of a vinyl ether in chemical reactions may be at least twofold, owing to its unsaturated nature and the presence of ether oxygen, which possesses marked onium properties [1,2,3,4]. To be sure, these functional properties do not exist in isolation but are manifested in combinations or accumulations, and as a result the behavior of the molecule will be much more complex than is expressed by the various notions and diagrams [5].

In studying the properties of vinyl alkyl ethers, the reciprocal bond between the functional groups and the individual atoms that constitute the molecule must be brought out. Investigation of the properties of vinyl alkyl ethers along this line enabled us to establish their peculiar behavior in a number of chemical transformations, partly protected us from the quite generally held view that these compounds are really derivatives of ethylene, and made it possible to approach the structure and properties of the products of halogenating [6,7] and hydrohalogenating [8] the original ethers.

The typical chemical properties of the vinyl alkyl ethers and their transformation can be conceived of much more clearly if they are compared with the chemical properties of the following vinyl compounds:

$CH_2{=}CHOH$; $CH_2{=}CHX$; $CH_2{=}CH{-}O{-}COR$; $CH_2{=}CH{-}R$,

where R is the respective alkyl or aryl group, and X is the halogen.

These vinyl compounds, which are classed together by a common nomenclature,

are generalized as substances whose properties are common to all of them. Yet there is no such thing as vinyl alcohol, and the vinyl ethers are the direct opposite of the hypothetical alcohol in point of stability.

The differences between the chemical properties of vinyl ethers and vinyl esters is most striking in their behavior toward halogens, hydrohalic acids, peroxides, and hydroperoxides.

The products of the halogenation and hydrohalogenation of vinyl ethers possess typical oxonium properties [9,10]: instability when acted on by water, light, or heat. Here we see the ability of the oxygen in vinyl alkyl ethers to exhibit oxonium properties as the result of intermolecular transformations (I), as well as of the constantly present mesomeric effect (II):

(I) $CH_2=CH-O-R + HX \longrightarrow [CH_2=CH-\underset{R}{O}H]X$

(II) $CH_2=CH-O-R \longleftrightarrow CH_2-\overset{H}{C}=\overset{+}{O}\overset{R}{}$

There is a sharp difference between the chemical properties of vinyl ethers and esters as manifested in their reactions with peroxides and hydroperoxides. The most typical and characteristic transformations of vinyl esters are effected by the action of peroxides, whereas the vinyl ethers do not tend to enter into such transformations.

The transformations of vinyl alkyl ethers are effected quite readily by mineral acids and metallic chlorides [11]. The action of mineral acids in these transformations has been established in the reactions of the vinyl alkyl ethers with halohydric acids:

$$CH_2=CH-O-R + HX \longrightarrow CH_3CHX-O-R.$$

The resulting molecule of the α-ethylalkyl halide is much more complicated and many-sided than is indicated by the classical formula. The concept of this molecule is broadened considerably if we bear in mind that the tautomeric effect of the original molecule after the hydrogen halide has been added, i.e., in the new molecule, acts in the opposite direction and results in the following tautomerism:

$$H-\overset{\frown}{CH_2}-\underset{Cl}{CH}-OR \rightleftharpoons CH_2=CH-\underset{HCl}{O}-R$$

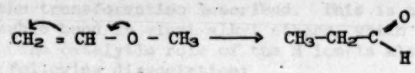
The existence of the α-ethylalkyl halides in the foregoing two tautomeric forms was propounded by me some years ago. This hypothesis was reinforced by the twofold nature of the behavior of these compounds, which give the impression of sometimes entering into a substitution reaction, while at others entering into addition reactions.

Consideration of the following tautomeric processes [12]:

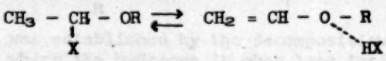
$$\overset{\frown}{CH_2}=\underset{H}{C}-\overset{\frown}{O}-H \rightleftharpoons CH_3-\overset{O}{\overset{\diagdown}{C}}_{H} \qquad R-CH_2-\underset{O}{\overset{H}{C}}-\overset{H}{C}-R \rightleftharpoons RCH_2-\underset{OH}{C}=CH-R$$

likewise leads to the same assumption.

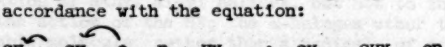
If the oxygen is not linked to hydrogen, but to some other positive radical, as, say in the molecule of vinyl methyl ether, this process of tautomerization is possible, but under more severe conditions, and it is apparently irreversible:



The foregoing makes the following representation of the tautomerism of α-ethylalkyl halides probable:



In the light of these notions of the structure and tautomerism of α-ethylalkyl halides, the problem of the possibility of forming a hydrogen bond or of adding halohydric acids solely in accordance with the equation:



becomes pointless.

Hence, the tautomerism of α-ethylalkyl halides arises from the very fact of the existence of a tautomeric effect in this system, the manifestation of which in one direction or the other results in the actual existence of the two forms mentioned above.

The reactions brought about by the manifestation of a tautomeric effect include the addition to vinyl alkyl ethers of substances that contain mobile hydrogen, as well as the opposite cleavage of the resulting addition products, as has been established in the following example, in particular.

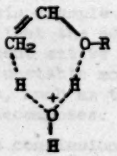
a) $CH_2 = CH - O - C_4H_9 + HOC_6H_5 \rightleftarrows CH_3CH(OC_4H_9)(OC_6H_5)$

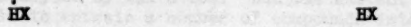
b) $CH_2 = CH - O - C_6H_5 + C_4H_9OH \longrightarrow CH_3CH(OC_4H_9)(OC_6H_5) \longrightarrow$

$\longrightarrow CH_2 = CH - O - C_4H_9 + C_6H_5OH$

In some cases, hydrogen bonds may appear simultaneously in Position 1 as well as in Position 3, i.e., with both the β-carbon atom and the oxygen atom in the vinyl alkyl ether; an instance of this sort is cited in our joint paper with E.N.Prilezhayeva and E.S.Shapiro [13].

When hydrohalide acids are added, the corresponding two outer positions may be as follows, likewise depending upon the nature of the hydrogen:





The process of establishing a hydrogen bond in these compounds is, in general, a negative factor, since an H-bond stabilizes the molecule by giving rise to a coordination compound and paralyzing its reactivity. A process of this sort occurs at

moderate temperatures (say, at room temperature or below); when heated the hydrogen bond is dissociated, and a tautomeric effect makes its appearance, impelling the molecule to undergo the transformation described. This is also related to the peculiarity of the double bond in vinyl alkyl ethers, which has an increased affinity for adding a proton. The catalytic role of the H ion is also related to this. I formerly assumed the following dissociation:

$$[CH_2 = CH - \underset{R}{O}H]X \longrightarrow CH_2 - \underset{|}{CH} - OR + HX,$$

but it applies, as was established by the decomposition of alkyl phenol acetals, only to complex ions in which the hydrogen is much less ionized than in mineral acids.

The catalytic role of halohydric acids in the conversions of vinyl alkyl ethers boils down to the formation of ethyl alkyl halides, but not to the polarization of the original ether by the action of the HX; the α-halogen ether then breaks down to form an activated unstable molecule, rather than a radical, of course, for otherwise biradicals and trimers would be formed; under certain conditions the following ion is apparently formed:

$$CH_3 - \underset{(Cl}{CH} - O - R \longrightarrow [CH_3 - CH = O^+ - R \longleftrightarrow CH_3 - \overset{+}{C}H - O - R]\bar{C}l$$

which readily adds OH, OR, OCOR, etc., or is the starting point of polymer chains.

When the components that can enter into chemical reaction with these α-halogen ethers are absent, the latter are readily decomposed in accordance with a different equation:

$$CH_3 - \underset{Cl}{CH} - OR \longrightarrow RCl + H_2O + \text{tar}.$$

It is obvious that this type of decomposition of α-ethylalkyl halides, which may be carried out exceptionally easily by the action of heat and light, has nothing in common with their catalytic role.

As has been said, the vinyl alkyl ethers are very readily polymerized by the α-ethylaklyl halides; here, too, the latter are decomposed, but an active complex ion is formed, which serves as the start of a polymer chain:

$$CH_3 - \overset{+}{C}H - O - R + CH_2 = CH - OR \longrightarrow CH_3 - \underset{OR}{CH} - CH_2 - \overset{+}{C}H - OR \quad \text{etc.}$$

This example of the processes of polymerization of vinyl alkyl ethers demonstrates that the addition and polymerization reactions take place here because of the nascent active molecule, which is catalyzed by the H ion. But the nascent activated unstable molecule is often unable to entrain a number of compounds into reaction, such as those that do not possess a mobile hydrogen atom, and then it simply decomposes.

In conclusion, let us dwell upon one more example, which shows the profound differences between the chemical nature of vinyl alkyl ethers and a number of vinyl compounds (vinyl acetate, alcohols, vinyl chloride, and the acrylates). We shall not touch on the mechanism of the activation of vinyl esters, in particular, but shall submit a table to demonstrate what has been set forth above.

TABLE 1

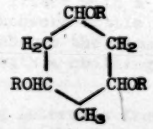
Factors and Reagents That Give Rise to the Polymerization of Vinyl Acetate, Vinyl Chloride, Styrene, Acrylates, and Vinyl Alkyl Ethers

Name of compound	Peroxides and hydroperoxides	Heating to from 60-80°	Sunlight	Atmospheric oxygen	Mineral acids
Vinyl acetate	+	+	+	+	−
Vinyl chloride	+	+	+	+	−
Styrene	+	+	+	+	−
Acrylates	+	+	+	+	−
Vinyl alkyl ethers	−	−	−	−	+

We therefore see that the tendency of all the above compounds to polymerize is a quite superficially general property of these compounds, inasmuch as the generality of their chemical properties does not follow from it. On the contrary, a detailed study of the processes of polymerizing the foregoing compounds indicates that the chemical properties of vinyl ethers and esters, in particular, are wholly different and that dissimilar factors and reagents are responsible for their chemical activation.

It should be added that the activated molecules formed by the action of peroxides or halohydric acids (in the case of the vinyl alkyl ethers) must by no means be identified as free radicals, inasmuch as they are incapable of di- or trimerization:

$$2CH_2 = CHOR \longrightarrow \begin{matrix} CH_2 - CHOR \\ | \quad\quad | \\ CH_2 - CHOR \end{matrix} \qquad 3CH_2 = \dot{C}HOR \longrightarrow$$



As for the feasibility of completely transforming the initial compounds into an activated state, we have shown this sufficiently convincingly [14] in our study of the conditions governing the reactions of the vinyl compounds with equimolecular quantities of halohydric acids and peroxides. Nor does dimerization take place in this case, notwithstanding the extraordinary abundance of activated molecules, but rather a far-reaching decomposition.

There must be difference in principle between the conditions for dimerization and those for polymerization.

EXPERIMENTAL

1. Synthesis of α-Bromoethyl Methyl Ether

$$CH_2{=}CH{-}O{-}CH_3 + HBr \longrightarrow CH_3CHBrOCH_3 \rightleftarrows [CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}OH]Br$$

37.5 g of methyl vinyl ether, possessing the following constants: b.p. 5-5.2° at 745 mm; n_D^0 1.3730; d_4^0 0.7723 [7]; was saturated with hydrogen bromide for 6 hours; the gain in weight was 44 g.

α-Bromoethyl methyl ether, 75.5 g (85% of the theoretical) was synthesized; it boils at 56.5-57° (158 mm) and has the following constants:

n_D^{20} 1.4486; d_4^{20} 1.4253; MR_D 26.11.

C_3H_7OBr. Computed: MR_D 25.46.
0.2010 g substance: 15.0 g benzene: Δt 0.52°.
0.4102 g substance: 15.0 g benzene: Δt 1.04°.
Found: M 132.0, 134.6.
C_3H_7OBr. Computed: M 138.9.
0.1360 g substance: 24.51 ml 0.1N $AgNO_3$; 14.74 ml NH_4CNS.
0.1566 g substance: 24.51 ml 0.1N $AgNO_3$; 13.26 ml NH_4CNS.
Found %: Br 57.06, 57.16.
C_3H_7OBr. Computed %: Br 57.54.

2. Synthesis of α,β-Dibromoethyl Methyl Ether

(Together with P.V.Tyupayev)

$$CH_2=CH-O-CH_3 + Br_2 \rightarrow CH_2BrCHBr-O-CH_3 \rightleftarrows [CHBr=CH-\underset{CH_3}{O}H]Br$$

We used 200.2 g of anhydrous bromine (b.p. 59°) and 72.9 g of anhydrous methyl vinyl ether (b.p. 5-6°). The apparatus consisted of a 500-ml three-necked flask with the following accessories connected to it via ground-in fittings: 1) a reflux condenser, through which there passed a stirrer; 2) a stopper that served as a jacket for a thermometer; and 3) a dropping funnel with a stopcock, fitted with an outer jacket and drain pipe for chilling with snow and an air connection with the reactor. The reflux condenser, through which ice water circulated, was fitted with a vent; the latter was connected via a calcium chloride tube to a Tishchenko bottle filled with a saturated solution of sodium thiosulfate, destined to absorb the bromine vapors. The reactor was placed in an aluminum kettle filled with a chilling mixture of snow and salt.

The methyl vinyl ether is added a drop at a time at long intervals from the dropping funnel with the stopper closed, care being taken to have the funnel jacket always filled with snow, to the bromine loaded into the reactor and chilled to -7°, with vigorous stirring and strong chilling. The synthesis is carried out at a temperature of the reaction mixture ranging from -10° to -3°. The reaction is exothermal. The synthesis is complete within 9 hours. During the addition of the first half of the methyl vinyl ether to the reactor the reaction is nearly two and a half times as slow as during the addition of the second half; white fumes are observed inside the reactor, accompanied by considerable crepitation, during the addition of the first half, whereas the addition of the second half of the ether takes place quietly, with the evolution of less heat. When an excess of ether is added, the temperature of the reaction mass does not rise, but continues to cool down to the temperature of the chilling mixture. This yields 272 g (99.7%) of a highly mobile, heavy, completely transparent, light-orange liquid, which fumes strongly in air and possesses rather marked lachrymatory properties. Fractionation in vacuum yielded:

Fraction 1,	27-56° (10 mm) –	16.4 g	
Fraction 2,	56° (10 mm) –	226.5 g	(83.3%)
Fraction 3,	56-69° (10 mm) –	5.6 g	
Residue		16.4 g	
Losses		7.1 g	

The principal, second, fraction has the following constants: d_4^{20} 1.9701; n_D^{20} 1.5300; MR_D 34.160. $C_3H_6OBr_2$. Computed: MR_D 33.227; exaltation 0.935.

After purification by means of repeated vacuum fractionation, this Fraction 2 had constants that agreed wholly with those stated. α,β-Dibromoethyl methyl ether boils at about 160° at standard pressure, but with considerable decomposition. Pure α,β-dibromoethyl methyl ether is a completely water-white, transparent, highly mobile heavy liquid, which can be kept excellently for very long periods without change either in a sealed ampoule or in a flask hermetically sealed with a rubber stopper.

3. Synthesis of Butyl Phenyl Acetal

(Together with N. A. Gershtein)

a) Synthesis of Butyl Phenyl Acetal from Butyl Vinyl Ether and Phenol

$$CH_2{=}CH{-}O{-}C_4H_9 + C_6H_5OH \rightarrow CH_3CH(OC_4H_9)(OC_6H_5)$$

48 g of phenol (0.5 mol) with a b.p. of 179-180° at 758 mm was mixed with 56.5 g of n-butyl vinyl ether (0.565 mol), i.e., with a slight excess of the latter. When the foregoing reaction components are mixed together, the temperature of the mixture is seen to drop. The room temperature was 14°; the initial reagents had the same temperature, but upon mixing them together, the temperature of the mixture dropped, to 4°. 0.05 g of 33% hydrochloric acid was added to the mixture, after which the contents of the flask were mixed together by shaking; the contents were found to warm up, the temperature rising rapidly to 86°. Then the mixture was left to stand overnight at room temperature. Double fractionation of the reaction mixture at reduced pressure yielded 80 g of a pure product that had the following constants:

b.p. 107-107.5° at 9 mm; d_{20}^{20} 0.9605; d_4^{20} 0.9588; n_D^{20} 1.4830; MR_D 57.67.
$C_{12}H_{18}O_2F$. Computed: MR_D 57.30.

0.2768 g substance: 24.46 g benzene: Δt 0.303°.
0.4360 g substance: 24.46 g benzene: Δt 0.483°.
Found: M 192.35, 190.1.
$C_{12}H_{18}O_2$. Computed: M 194.
5.560 mg substance: 15.088 mg CO_2; 4.595 mg H_2O.
Found %: C 74.01; H 9.24.
$C_{12}H_{18}O_2$. Computed %: C 74.22; H 9.28.

b) Synthesis of Butyl Phenyl Acetal from Phenyl Vinyl Ether and Butanol

$$CH_2{=}CH{-}O{-}C_6H_5 + C_4H_9OH \rightarrow CH_3CH(OC_6H_5)(OC_4H_9)$$

60 g of phenyl vinyl ether and 40 g of butanol (an equimolar mixture) were heated for 10 hours to 170-180° in a revolving autoclave. The pressure inside the autoclave was found to be about 2 atm. Fractionation of the reaction products yielded the following results:

Fraction 1,	95-118° (18 mm)	22.5 g
Fraction 2,	121-121.5° (15 mm)	59.1 g
Fraction 3,	150.5-154° (15 mm)	9 g

Further fractionation of Fraction 1 yielded dibutyl acetal and phenol. Refractionation of Fraction 2 proved it to be the product sought after, with the following constants:

b.p. 121-121.5° at 15 mm and 115-116° at 12 mm; d_{20}^{20} 0.9600; d_4^{20} 0.9582; n_D^{20} 1.4840; MR_D 57.91. $C_{12}H_{18}O_2F$. Computed: MR_D 57.30.

After redistillation Fraction 3 had the following constants:
B.p. 148.5-149.5° at 12 mm; d_4^{20} 1.087; n_D^{20} 1.5568; MR_D 63.34.

$C_{14}H_{14}O_2F$. Computed: MR_D 62.94.

0.150 g substance: 12.25 g benzene: Δt 0.3065°.
Found: M 205.
$C_{14}H_{14}O_2$. Computed: M 214.

3.708 mg substance: 10.656 mg CO_2; 2.188 mg H_2O.
5.248 mg substance: 15.085 mg CO_2; 3.092 mg H_2O.
Found %: C 78.43; 78.44; H 6.67, 6.54.
$C_{14}H_{14}O_2$. Computed %: C 78.51; H 6.54.

4. Synthesis of Butyl-β-Naphthyl Acetal

Because of the poor solubility of β-naphthol in butyl vinyl ether, twice the theoretical quantity of the latter was used. A catalyst – 0.05 g of 33% hydrochloric acid – was added to a mixture consisting of 36 g (0.25 mol) of β-naphthol with a m.p. of 95-96° and 50 g (0.5 mol) of n-butyl vinyl ether, which is a thin slurry at room temperature (14°). The temperature of the mixture then began to rise slowly to 32°. The reaction mass turned into a dark-red mobile liquid. The mixture was set aside to stand overnight. Then the mixture was diluted with sulfuric ether, washed with a concentrated potash solution to neutralize the catalyst, and desiccated over calcined potash. The product was distilled in vacuum after the ether had been driven off. Fractionation yielded the following fractions:

Fraction 1, b.p. 25° at 16 mm – 22 g.
Fraction 2, b.p. 25-180° at 16 mm – 2.0 g.
Fraction 3, b.p. 183.5-185° at 16 mm – 58 g; n_D^{20} 1.5538.

Fraction 1 is the original butyl vinyl ether, which had a b.p. of 93.5-93.8° when distilled at standard pressure; n_D^{20} 1.4028. Refractionation of Fraction 3 yielded the following results:

B.p. 187.2-187.4° at 16 mm; d_{20}^{20} 1.0543; d_4^{20} 1.0521; n_D^{20} 1.5548; MR_D 74.44.
$C_{16}H_{20}O_2F_5$. Computed: MR_D 72.641.

55.1 g of this fraction was collected, which represented a yield of 90.3% of the theoretical in terms of β-naphthol.

5. Thermal Cleavage of Alkyl Aryl Acetals:

$$CH_3CH(OAlk)(OAr) \rightarrow CH_2{=}CH{-}OAlk + ArOH$$

The cleavage of acetals has been investigated by many authors under different conditions, both in order to synthesize vinyl ethers and to pyrolyze them. What interested us was the nature of the decomposition of alkyl aryl acetals under comparatively mild conditions, i.e., during distillation at normal pressure. We chose butyl phenyl acetal as the subject of our research. The thermal cleavage of the acetal was effected by heating it in a Favorsky flask at atmospheric pressure. In Experiment 1, we used 19.5 g of butyl phenyl acetal and obtained the following fractions under the specified conditions:

Fraction 1,	92-132° –	8.6 g
Fraction 2,	175-177° –	1.2 g
Fraction 3,	178-198° –	6.0 g
Residue in the flask	–	3.5 g
	Total	19.3 g
	Losses	0.2 g

In Experiment 2, we used 31.8 g of this acetal and obtained the following results:

Fraction 1,	92-135° –	8.9 g
Fraction 2,	136-175° –	10.3 g (most at 175°)
Fraction 3,	180-238° –	8.9 g
Residue in the flask	–	3.0 g
	Total	31.1 g
	Losses	0.7 g

The corresponding fractions collected in both experiments were combined and fractionated further. The refractionation of Fraction 1 yielded:

1) Butyl vinyl ether – b.p. 92.5-95.5° (752 mm); d_4^{20} 0.7788; n_D^{20} 1.4020;

2) Butanol with a b.p. of 115.5-117° (750 mm); n_D^{20} 1.400;

3) Phenol with a b.p. of 181-183° (752 mm); n_D^{20} 1.4158.

Repeated fractionation of the combined fractions 2 of the foregoing experiments yielded a substance with a b.p. of 176-177°. This fraction crystallized completely and proved to be phenol (4.2 g).

Fraction 3 distilled over the range of 178-187° (n_D^{20} 1.5450) and proved to be a mixture of dibutyl acetal and phenol. This mixture was diluted with absolute ether and treated with metallic sodium. Driving off the ether from the filtrate of alcoholates yielded a small quantity of a product with a b.p. of 185-187° and n_D^{20} 1.4095, which was not analyzed any further.

6. Synthesis of Ethyl Phenyl Acetal

(Together with A.V.Bogdanova)

$$CH_2{=}CH{-}OC_2H_5 + C_6H_5OH \longrightarrow CH_3{-}CH\begin{matrix}OC_2H_5\\OC_6H_5\end{matrix}$$

95 g of ethyl vinyl ether (b.p. 36°; n_D^{20} 1.3775) and 124 g of phenol (b.p. 181-181.5°) were placed in a revolving autoclave with a capacity of 500 ml and heated to 125-130° for 7 hours. The maximum pressure in the autoclave was found to be 5.5 atm. After cooling, 216 g of a transparent, yellow reaction mass was discharged from the autoclave. The reaction products were fractionated in vacuum, yielding the following fractions:

Fraction 1, 85-91° at 18 mm	6 g
Fraction 2, 91-92° at 18 mm	186 g
Fraction 3, 92-98° at 18 mm	5 g

Fraction 2 was analyzed further. After refractionating it, the constants of the substance recovered were: b. p. 91-92°; $n_D^{21.5}$ 1.5050; $d_4^{21.5}$ 0.99. Hence, the product recovered proved to be ethyl phenyl acetal, with constants that are close to those specified in the literature [15].

7. Thermal Decomposition of Ethyl Phenyl Acetal

92.5 g of ethyl phenyl acetal was decomposed thermally by distilling it slowly from a Favorsky flask (with a dephlegmator) at atmospheric pressure. The product was heated over Wood's metal. In addition to the condenser, the distilling apparatus was fitted with several receivers for collecting the liquid and gaseous products. The following fractions were collected:

Fraction 1, 34-67°	12.3 g
Fraction 2, 67-83°	15.5 g
Fraction 3, 83-176°	0.6 g
Fraction 4, 176-193°	37 g
Fraction 5, 193-210°	4 g
Residue in the flask	22 g.

Treatment of Fraction 1 yielded ethyl vinyl ether, with the following constants: b.p. 36°; n_D^{20} 1.3770; d_4^{20} 0.7538. Double fractionation of Fraction 2 yielded ethyl alcohol: b.p. 78°; $n_D^{21.5}$ 1.3625. Refractionation of Fraction 4 yielded in the main a substance with a b.p. of 181-182°. The product collected proved to be phenol, which crystallized and had a m.p. of 37°. When this product was mixed with an alcoholic solution of bromine, a precipitate of tribromophenol was recovered. Careful treatment of Fraction 5 yielded diphenyl acetal, possessing the following constants: b.p. 128-130° at 20 mm; n_D^{20} 1.5500; d_4^{20} 1.0857. The 22 g of residue in the flask turned into a brittle dark mass with a strong odor of phenol.

8. Investigation of the Polymerization of Vinyl Alkyl Ethers by α-Halogen Ethers

a) 50 g of butyl vinyl ether is placed in a 75-ml ampoule, and 2 g of α-chloroethyl butyl ether is added with constant stirring. Then the ampoule is sealed and placed in a cabinet to keep out the light. The ampoule is stored at room temperature. Under these conditions the process of polymerization is extremely slow, a detectable amount of the polymer being formed only after 2 to 3 months have elapsed. Then the contents of the ampoule are dissolved in acetone, and the polymer is precipitated with ethyl alcohol. This treatment yields a polymer with the following constants: n_D^{20} 1.4535; d_4^{20} 0.9238; M 1200.

b) 50 g of butyl vinyl ether was placed in a 150-ml three-necked flask fitted with a mechanical stirrer and a reflux condenser, and 2 g of α-chloroethyl butyl ether was added. The mixture was heated over a boiling water bath. The progress of the polymerization reaction was checked by determining the refractive index of the reaction mixture at 30-minute intervals. As shown in Table 2, the reaction takes place much faster when the reagents are heated than is the case in the experiments described under a) above.

TABLE 2

Time	Temperature of the reaction medium	n_D^{20}	Time	Temperature of the reaction medium	n_D^{20}
10 h., 30 min	95°	1.4020	12 h, 30 m.	95°	1.4240
11 h., 00 min	95	1.4052	13 h, 00 m.	98	1.4370
11 h., 30 min	95	1.4130	13 h, 30 m.	98	1.4460
12 h., 00 min	95	1.4192	14 h, 00 m.	98	1.4485

c) 50 g of butyl vinyl ether and 2 g of dibromoethyl butyl ether were placed in a 75-ml ampoule. The reaction mixture was exposed to the action of direct sunlight. A noticeable increase in the viscosity of the reaction mixture was observed after no more than 6 to 8 hours, polymerization being complete after 3 to 4 days.

9. Investigation of the Mechanism of Activation of Butyl Vinyl Ether by α-Bromoethyl Phenyl Ether

19.8 g of α-bromoethyl phenyl ether (b.p. 88-89° at 7 mm; $n_D^{21.5}$ 1.5500) was placed in an ampoule, and 10 g of butyl vinyl ether and 20 g of dioxane were added. Direct sunlight was allowed to fall on the reaction mixture. The mixture turned yellow after two days had passed, and an amorphous deposit settled out. The mixture was then kept one more day, after which it underwent suitable treatment and separation. The precipitate was filtered out, and the filtrate was fractionated. The first fraction to be collected was 27.9 g of a 93-101° fraction, an undistilled polymer with a sharp phenol odor remaining in the flask. The 93-101° fraction quickly separated into two layers. After these layers had been separated – the lower layer totaling 8.2 g, and the upper one 19.7 g – they were identified. The lower layer proved to be butyl bromide (b.p. 100-102°; n_D^{18} 1.4400; d_4^{20} 1.2780), while the upper layer was a mixture of water and dioxane.

SUMMARY

1. α-Ethyl alkyl halides and the corresponding α,β-halogen derivatives exist in two tautomeric forms:

$$H\text{-}CH_2\text{-}\underset{X}{CH}\text{-}O\text{-}R \rightleftarrows CH_2\text{=}CH\text{-}O\text{-}\underset{HX}{R}$$

2. In chemical reactions, the α-ethyl alkyl halides react ionically, forming a mesomeric ion:

$$CH_3\text{-}\underset{X}{CH}\text{-}O\text{-}R \longrightarrow [CH_3\overset{+}{C}H\text{-}O\text{-}R \longleftrightarrow CH_3\text{-}CH\text{-}O\overset{+}{R}]\overline{X}$$

3. α-Ethyl alkyl halides act as catalysts in the transformations of vinyl alkyl ethers; the decomposition of the latter is then ionic and irreversible.

4. The products of the addition of phenol to vinyl alkyl ethers decompose reversibly:

$$CH_2\text{=}CH\text{-}OR + C_6H_5OH \rightleftarrows CH_3\text{-}CH(OR)(OC_6H_5);$$

a) Phenol is readily split off during the thermal decomposition of alkyl aryl acetals, the corresponding alkyl vinyl ether being formed;

b) Under the reaction conditions, the accumulating phenol in the reaction mass of alkyl aryl acetals displaces the corresponding aliphatic alcohol, resulting in the synthesis of diaryl acetals.

5. The action of direct sunlight and heating facilitate the decomposition of α-dialkyl and α-alkyl aryl halides.

6. The chemical properties of vinyl alkyl ethers are due to the peculiar combination of the double bond and the ether oxygen, which possesses onium properties.

LITERATURE CITED

[1] M.F.Shostakovsky, J. Gen. Chem., 13, 674 (1943).

[2] M.F.Shostakovsky, Doklady. USSR Acad. Sci., 41, 124 (1943).

[3] N.A.Gershtein and M.F. Shostakovsky, J. Gen. Chem., 18, 451 (1948).

[4] C.W.Mortenson, M.A.Spielman, J.Am. Chem. Soc.., 62, 1609 (1940).

[5] M.F.Shostakovsky and E.N.Prilezhayeva, J. Gen. Chem., 17, 1129 (1947).

[6] M.F.Shostakovsky and M.G.Voronkov, J. Gen. Chem., 14, 102 (1944).

[7] M.F.Shostakovsky, Yu.B.Kagan, and F.P.Sidelkovskaya, J.Gen. Chem., 17, 957, (1947).

[8] M.F.Shostakovsky and A.V.Bogdanova, J.Gen.Chem., 17, 565 (1947).

[9] Ch. Friedel, Bull. Soc. chim., 24, 160 (1875).

[10] V.V.Chelintsev. Organic Catalysts (Monograph, 1939).

[11] M.F.Shostakovsky and F.P.Sidelkovskaya, J.Gen.Chem., 13, 428 (1943).

[12] C.E.Schildknecht, A.P.Zoss, Clyde, McKinley, Ind. Eng. Chem., 39 (1947).

[13] E.N.Prilezhayeva, E.S.Shapiro, and M.F.Shostakovsky, J.Gen.Chem., 18, 1663 (1948).

[14] M.F.Shostakovsky, Vestnik USSR Acad. Sci., No. 12, 13 (1948); M.F.Shostakovsky. Research on High Molecular Compounds, p. 34 (1949), USSR Acad. Sci. Press.

[15] E. P. 352472, 1930; Zbl., 1931, II, 2757.

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THE ACTION OF INORGANIC BASES UPON α, β, DICHLOROETHYL ALKYL ETHERS

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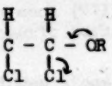
In one of our reports [1] we have described the synthesis of α,β-dichloroethyl butyl and α,β-dichloroethyl isoamyl ethers by chlorinating vinyl ethers. The properties of α,β-dichloro ethers are of considerable interest, because of the sharp difference between the behavior of the α- and β-chlorine atoms. Whereas the chlorine atom in the alpha position with respect to the alkoxy group is extremely mobile, enters readily into exchange reactions, is detached as hydrogen chloride, and (like the α-halogen in α-halogen ethers [2]) has properties that closely resemble those of the ionic halogen in inorganic salts, the chlorine in the β-position is quite inert and has properties that resemble those of the halogen in ordinary organic halides. This singular behavior of α,β-dichloroethers cannot be satisfactorily explained merely by the classical covalent formula. The presence of an oxygen atom entails a mesomeric effect for the α,β-dichloroethers.

(I)

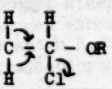


This concept of the structure of α,β-dichloroethers provides a good explanation for the difference in the behavior of the two atoms of chlorine.

Another peculiarity of α,β-dichloroethers is the increased mobility of the β-hydrogen atoms, which can be replaced by a chlorine atom, and can also be detached as hydrogen chloride by heating the compound with tertiary aliphatic-aromatic amines [1].

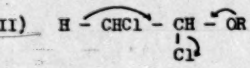
This phenomenon may be due to the fact that the α-atom of chlorine partially saturates its electronegativeness at the expense of the β-hydrogen atoms, making the latter more positive and hence more active. Hence, we must bear Formula (II) in mind:

(II)



as well as Formula (I). Thus, a fuller characterization of α,β-dichloroethers

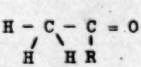
demands that their structure be represented by the following formula:

(III) 

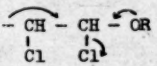
Such an electron displacement may upset and shatter the bonds so much that tautomerism may set in, with a shift of the active β-hydrogen to the oxygen atom. The dichloro ether then becomes an equilibrium mixture of two tautomeric forms, as has been suggested by us earlier [1]:

(IV) $CH_2Cl - CHCl - OR \rightleftharpoons \left[CHCl = CH - O(H) - R\right]^{+}Cl^{-}$

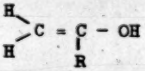
Formally, we may cite the analogy with ketol-enol tautomerism:

(V) 

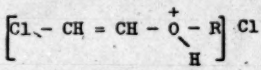
ketone

(VI) 

dichloro ether

(VII) 

enol

(VIII) 

oxonium form of an α,β-dichloro ether

The well-known activity of the α-hydrogen in carbonyl compounds and the activity of β-hydrogen in α,β-dichloro ethers are due to the contracting of the electrons about the carbonyl oxygen (V) in the former case and about the α-chlorine (VI) in the latter. Under certain conditions this hydrogen may separate out as a proton, resulting in formation of the enol (VII) or the oxonium (VIII) tautomeric form, respectively. The two tautomeric forms (VI and VIII) may explain the reactivity of α,β-dichloroethers.

Study of the behavior of halogen atoms with organic and inorganic bases may be one way of determining the degree of activity of these atoms. There are references in the literature to the reaction of halogenated ethers with alkaline agents. But they deal, in the main, with ethers in which the halogens are in the β- or γ-position to the alkoxy group. In these instances, the hydrogen halides are split off, and compounds with multiple bonds are formed. Cretcher and his associates [3,4], for instance, produced divinyl ether by heating β-β-dichloroethyl ether with sodium hydroxide. Acetaldehyde and 1,4-dioxane were by-products. Ruigh and Major [5] synthesized divinyl ether by reacting this same compound with fused caustic potash at 250°. They secured acetaldehyde and large quantities of gases (hydrogen, acetylene, and other hydrocarbons) as by-products. Using sodium amide or calcium oxide yielded the same results. Henry [6] synthesized the compound $CH_2{=}CBr{-}CH_2{-}OCH_3$ by distilling methyl-β,γ-dibromopropyl ether over solid sodium hydroxide. As for the action of bases upon α,β-dihalogen ethers, the sole reference thereto is contained in a paper by A.E.Favorsky and M.N.Shchukin [7], who secured bromoacetal by reacting potassium hydroxide with α,β-dibromoethyl alkyl ethers in absolute ether.

In our research we used an alcoholic solution of caustic potash and anhydrous potassium hydroxide, metallic sodium, gaseous ammonia, calcium oxide, and potash.

Whenever these reagents acted upon α,β-dichlorobutyl ether, dibutyl chloroacetal, $CH_2Cl-CH(OC_4H_9)_2$, described by us previously, was produced, instead of the expected β-chlorovinyl butyl ether. To determine the mechanism of the reaction it was desirable to establish the part played by the alcohol that is present in the reaction mixture as a solvent for the alkali. This was accomplished by carrying out the reaction with sodium hydroxide dissolved in butyl and heptyl alcohol. When butanol was used, we recovered dibutyl chloroacetal (with a yield of 55%); using heptanol, we synthesized butyl heptyl chloroacetal for the first time:

$$CH_2Cl - CH\begin{matrix}OC_4H_9\\OC_7H_{15}\end{matrix}$$

(with a yield of 39%) and diheptyl chloroacetal, $CH_2Cl - CH(OC_7H_{15})_2$ (with a yield of 14%).

The mechanism of the reaction in which the chloroacetals are formed by the action of inorganic bases upon the α,β-dichloroethers may differ, depending upon the reagent used.

1. When alcohols or alcoholic alkalies are used, the end products are formed by the substitution of an alkoxy group for the α-chlorine, as follows:

$$\text{(IX)}\quad CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + R'OH \longrightarrow CH_2Cl-CH\begin{matrix}OR\\OR'\end{matrix} + HCl$$

or

$$\text{(X)}\quad CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + R'OH + NaOH \longrightarrow CH_2Cl-CH\begin{matrix}OR\\OR'\end{matrix} + NaCl + H_2O.$$

The formation of diheptyl chloroacetal by the action of sodium hydroxide upon dichloroethyl butyl ether in heptyl alcohol may be explained as a disproportionation reaction of the initially formed butyl heptyl acetal. Reference is repeatedly made to the possibility of disproportionation in the series of unhalogenated mixed acetals in papers by M.F.Shostakovsky and N.A.Gershtein [8,9].

2. The action of fused alkali, gaseous ammonia, potassium carbonate, and calcium oxide involves the binding of the chlorine and hydrogen ions. The unsaturated radical that results is unstable and breaks down at once, yielding an alcohol and a tarry substance. The alcohol reacts with the initial α,β-dichloroether as indicated in (IX) above. We still do not know what the tarry substance is; it may be a polymer of chloroacetylene. We shall denote it by the minimum formula (C_2HCl).

$$\text{(XI)}\quad CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + NaOH \longrightarrow NaCl + H_2O + ROH + C_2HCl$$

$$\text{(XII)}\quad 2CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + K_2CO_3 \longrightarrow 2KCl + 2ROH + CO_2 + H_2O + 2C_2HCl$$

$$\text{(XIII)}\quad 2CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + CaO \longrightarrow CaCl_2 + H_2O + 2ROH + 2C_2HCl$$

$$\text{(XIV)}\quad CH_2Cl-\underset{\displaystyle Cl}{\underset{|}{CH}}-OR + NH_3 \longrightarrow NH_4Cl + ROH + C_2HCl$$

In Reactions (XI), (XII), and (XIII), water is evolved during the reaction; the water also reacts with dichloroethers to form chloroacetals, as pointed out in our preceding paper [1].

3. The reaction of the dichloroethers with metallic sodium is a somewhat special case. A chlorine ion is detached, after which the resulting free radical breaks down:

$$\text{(XV)}\quad CH_2Cl{-}\underset{Cl}{CH}{-}OR + Na \longrightarrow NaCl + CH_2Cl{-}\underset{\cdot}{CH}{-}OR \longrightarrow C_2HCl + ROH + H$$

The yield of chloroacetal in these reactions depends on the nature of the alkaline agent (see the table below).

EXPERIMENTAL

The initial α,β-dichloroethyl butyl ether used in this research had the following constants: b.p. 51-52° (7 mm); n_D^{20} 1.4475; d_4^{20} 1.1020.

1. Reaction of α,β-dichloroethyl butyl ether with potassium hydroxide. a) 9 g of potassium hydroxide was added in several batches to 29 g of the dichloroether. This caused the temperature to rise to 50° and the exterior of the potassium hydroxide to turn yellow. Then the reaction mass was heated to 70-80° for 16 hours. The solid precipitate was filtered out and washed with sulfuric ether. The ether extract was combined with the bulk product; after the ether had been driven off, fractionation yielded 1 g of the dichloroether with a b.p. of 114-116° at 14 mm (90% of the theoretical) plus a small quantity of tar. After triple fractionation the dibutyl chloroacetal possessed the following constants: b.p. 113-114° (13 mm); d_4^{20} 0.9620; n_D^{20} 1.4320; MR_D 56.79. $C_{10}H_{21}O_2Cl$. Computed: MR_D 56.27.

Yield of Chloroacetal in the Reaction of α,β-Dichloroethyl Butyl Ether with Alkaline Agents

Alkaline agent	Chloroacetal output (% of theoretical)
Metallic sodium*	24
Gaseous ammonia*	33
Calcium oxide*	51
Potash*	63
KOH + butanol	53
KOH + heptanol**	53
Anhydrous potassium hydroxide*	90

0.1458 g substance: 15.20 g benzene: Δt 0.255°.
0.2356 g substance: 15.00 g benzene: Δt 0.410°.
Found: M 198, 202.
$C_{10}H_{21}O_2Cl$. Computed: M 208.5.

b) 1 g of potassium hydroxide (9% by weight of the dichloroether) was added to 33 g of the dichloroether. This raised the temperature to 30°. The subsequent procedure was the same as in Experiment a). This yielded 10 g (55% of the theoretical) of the unreacted dichloroether, 4.5 g of dibutyl chloroacetal (b.p. 112-113° at 12 mm; n_D^{20} 1.4315), and 3 g of tar. The chloroacetal yield was 8%, i.e., in agreement with the quantity of alkali (9%) used for the reaction. These figures indicate that KOH is not a catalyst, but participates in the process in quantities that correspond to the stoichiometrical equation.

2. Reaction of α,β-dichloroethyl butyl ether with potassium hydroxide in butyl alcohol. 25 g of the dichloroether was added drop by drop, with constant stirring,

*The output (in % of the theoretical) is given as computed from the stoichiometrical equation.
**This percentage is the overall output of butyl heptyl and diheptyl acetals.

to a flask containing 12 g of potassium hydroxide dissolved in 20 g of butyl alcohol (b.p. 117-118°; n_D^{20} 1.3990). The mixture grew warm (the temperature rising to 40°), and a white crystalline powder – potassium chloride – was formed. The crystals were filtered out and washed with ether. Driving off the ether and subsequent fractionation yielded 16 g of butyl alcohol with a b.p. of 117-117.5°, n_D^{20} 1.4000, and 16 g of dibutyl chloroacetal (53% of the theoretical) with a b.p. of 107-108° (10 mm); n_D^{20} 1.4317; d_4^{20} 0.9650.

3. Reaction of α,β-dichloroethyl butyl ether with potassium hydroxide in heptyl alcohol. 30 g of the dichloroether were added drop by drop to 10 g of potassium hydroxide in 20 g of heptyl alcohol (b.p. 174-176°; n_D^{20} 1.4235). Inasmuch as the reaction resulted in the evolution of considerable heat, the reaction flask was water-cooled. Toward the end of the reaction the flask contents were heated for 4 hours to 60-70° over a water bath. The solid precipitate that settled out was filtered out and washed with sulfuric ether. The ether extract was combined with the bulk of the substance, which consisted of two layers: an aqueous and an ethereal one.* After the ether had been driven off, the following fractions were collected:

Fraction 1:	39-45° (28 mm)	4 g;	n_D^{20} 1.4125;
Fraction 2:	50-115° (15 mm)	6 g;	n_D^{20} 1.4290;
Fraction 3:	115-155° (15 mm)	5 g;	n_D^{20} 1.4320;
Fraction 4:	155-170° (15 mm)	20 g;	n_D^{20} 1.4360;
Fraction 5:	170-190° (15 mm)	10 g;	n_D^{20} 1.4400.

Repeated fractionation of the Fractions 3, 4, and 5 recovered 17 g (39% of the theoretical) of butyl heptyl chloroacetal - $CH_2Cl-CH(OC_4H_9)(OC_7H_{15})$ with a b.p. of 157-160° (17 mm), and 7 g (14% of the theoretical) of diheptyl chloroacetal $CH_2Cl-CH(OC_7H_{15})_2$, with a b.p. of 187-190° (17 mm). We should have recovered dibutyl chloroacetal as well (on the assumption that diheptyl chloroacetal is a disproportionation product of butyl heptyl chloroacetal). It was not obtained in the pure state, though it may have been present in Fraction 2, which did not undergo detailed analysis.

The Butyl heptyl chloroacetal had the following constants: b.p. 159° (16 mm); n_D^{20} 1.4367; d_4^{20} 0.9337; MR_D 70.06. $C_{13}H_{27}O_2Cl$. Computed: MR_D 70.01.

4.203 mg substance: 2.569 mg AgCl.
6.323 mg substance: 3.810 mg AgCl.
3.949 mg substance: 9.139 mg CO_2; 3.796 mg H_2O.
3.220 mg substance: 7.409 mg CO_2; 3.115 mg H_2O.
Found %: C 62.16, 62.31; H 10.85, 11.07; Cl 15.2, 14.91.
$C_{13}H_{27}O_2Cl$. Computed %: C 62.11; H 10.80; Cl 14.17.

0.1464 g substance: 20.6 g benzene: Δt 0.150°.
0.2898 g substance: 20.6 g benzene: Δt 0.290°.
Found: M 249.1, 255.4.
$C_{13}H_{27}O_2Cl$. Computed: M 250.5.

Diheptyl chloroacetal had the following constants: b.p. 188-188.5° (17 mm); n_D^{20} 1.4420; d_4^{20} 0.9247; MR_D 83.70. $C_{16}H_{33}O_2Cl$. Computed: MR_D 83.86.

5.720 mg substance: 2.858 mg AgCl.
6.930 mg substance: 3.523 mg AgCl.
4.255 mg substance: 10.229 mg CO_2; 4.145 mg H_2O.
4.485 mg substance: 10.808 mg CO_2; 4.435 mg H_2O.
Found %: C 65.61, 65.76; H 10.90, 11.06; Cl 12.36, 12.57.
$C_{16}H_{33}O_2Cl$. Computed %: C 65.30; H 11.28; Cl 12.13.

*The etheral layer was separated out and dessicated.

0.1464 g substance: 17.5 g benzene: Δt 0.152°.
0.2890 g substance: 17.5 g benzene: Δt 0.300°.
Found: M 290.3, 289.0.
$C_{16}H_{33}O_2Cl$. Computed: M 292.5.

4. Reaction of α,β-dichloroethyl butyl ether with calcium oxide. 54 g of the dichloroether was added to 25 g of calcium oxide. Theoretically, 9 g of calcium oxide is needed to split off hydrogen chloride. The excess calcium oxide was used to absorb the water that was set free. The reaction mixture was heated for 15 hours to 70-75°. The solid precipitate was filtered out and washed with sulfuric ether. The ether extract was added to the bulk product, and the aggregate was desiccated over sodium sulfate. After the ether had been driven off, fractionation yielded 14 g (20%) of the dichloroether that had not entered into the reaction, 17 g (51% of the theoretical) of dibutyl chloroacetal (b.p. 123-124° at 17 mm; n_D^{20} 1.4320; d_4^{20} 0.9675), and 6 g of tar.

5. Reaction of α,β-dichloroethyl butyl ether with potash. 30 g of the dichloroether and 7 g of calcined potash were heated to 70-80° for 20 hours with a reflux condenser over a water bath. The solid precipitate, which was a mixture of the potash and calcium chloride, was filtered out and washed with sulfuric ether. Driving off the ether and fractionation yielded 6.5 g (21.6%) of the unreacted dichloroether, 10 g (65 % of the theoretical) of dibutyl chloroacetal (b.p. 122-123° at 16 mm; n_D^{20} 1.4320; d_4^{20} 0.9668), and 3 g of tar.

6. Reaction of α,β-dichloroethyl butyl ether with gaseous ammonia. 30 g of the dichloroether was placed in a flask fitted with a reflux condenser and a stirrer, and a current of anhydrous ammonia (desiccated with a solid alkali) was passed through. Within 20-30 minutes the formation of white precipitate of ammonium chloride was noted, and the reaction mass heated up to 50°. The ammonia current was turned off when the contents of the flask had been turned into a compact, solid, yellow mass. The solid precipitate (6 g) was filtered out and washed with sulfuric ether. The ether extract was added to the bulk product. Driving off the ether yielded 6 g (17%) of the unreacted dichloroether, 6 g (33% of the theoretical) of dibutyl chloroacetal (b.p. 118-119° at 16 mm; n_D^{20} 1.4318; d_4^{20} 0.9662), and a little tar. The yellow residue (ammonium chloride) was recrystallized from hot water and identified by its ammonium and chlorine ions.

7. Reaction of α,β-dichloroethyl butyl ether with metallic sodium. At room temperature metallic sodium reacts extremely slowly with α,β-dichloroethyl butyl ether; only after 5-6 days, for example, did we note an insignificant resinification of the liquid and the appearance of a black film upon the surface of the sodium. But heating the dichloroether with sodium resulted in a violent reaction and tarring of the ether, so that the reaction was carried out by means of heating in benzene: 28 g of the dichloroether in 55 g of anhydrous benzene was heated for 6 hours to 70-80° with metallic sodium. The sodium turned into a brown resinified substance. Filtration of the deposit and driving off the benzene yielded 25% of the unreacted dichloroether and 4 g of dibutyl chloroacetal (24% of the theoretical), with a b. p. of 106-108° at 10 mm; n_D^{20} 1.4320.

SUMMARY

1. The reaction of α,β-dichloroethyl butyl ether with metallic sodium, gaseous ammonia, potash, calcium oxide, potassium hydroxide, and an alcoholic solution of potassium hydroxide has been studied. In every case the reaction product proved to be dibutyl chloroacetal.

2. Butyl heptyl chloroacetal and diheptyl chloroacetal have been synthesized by the reaction of potassium hydroxide and heptyl alcohol with α,β-dichloroethyl butyl ether.

3. The mechanism of the reaction between α,β-dichloroethyl butyl ether and alkaline reagents is given; it consists of detaching hydrogen and chlorine ions, followed by decomposition of the resulting unstable molecule and the evolution of an alcohol, which reacts with the original dichloroether to form the chloroacetal.

LITERATURE CITED

[1] M.F.Shostakovsky, Yu.B.Kagan, and F.P.Sidelkovskaya, J.Gen.Chem., 17, 957 (1947).

[2] M.F.Shostakovsky and A.V.Bogdanova, J.Gen.Chem., 17, 365 (1947).

[3] L.H.Cretcher, J.A.Koch, and W.H.Pittenger, J. Am. Chem. Soc., 47, 1173-1177 (1925).

[4] L.H.Cretcher and W.H.Pittenger, J.Am. Chem. Soc., 47, 163-166, (1925).

[5] W.L.Ruigh and R.T.Major, J. Am. Chem. Soc., 53, 2662-2671 (1931).

[6] L. Henry, Ber., 5, 455 (1872).

[7] A.E.Favorsky and M.N.Shchukina, J.Gen.Chem., 15, 385 (1945).

[8] M.F.Shostakovsky and N.A.Gershtein, J.Gen.Chem., 16, 937 (1946).

[9] M.F.Shostakovsky and N.A.Gershtein, J.Gen.Chem., 18, 115 (1948).

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RESEARCH IN THE FIELD OF FURAN DERIVATIVES

I. SYNTHESIS AND SOME PROPERTIES OF FURYLACROLEIN AND FURYL ALLYL ALCOHOL

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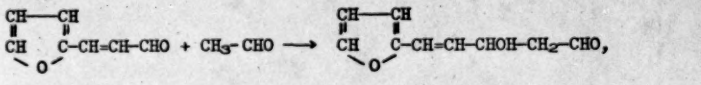
The present paper sets forth experiments on the synthesis of furylacrolein and its reduction to the little known furyl allyl alcohol.

As we know, furylacrolein is synthesized by condensing furfural with acetaldehyde in the cold in the presence of dilute caustic alkali. The differences found in the procedures described in the literature comprise changes in the quantity of alkali or of acetaldehyde used and in the order in which the reagents are added [1,2,3]. As a rule, a large excess of acetaldehyde is used; in Konig's procedure [1], for instance, the excess of acetaldehyde is as much as 75% of what is theoretically required. The fundamental defect in the procedures given is the absence of detailed examination of this reaction, particularly a study of the side reactions and an elucidation of the reasons for their appearance. Besides the basic condensation reaction, other side reactions may be expected to occur, effectively reducing the output of furylacrolein. First of all, dismutation of the furfural may take place. But, owing to the low alkali concentration and the low temperature, this latter reaction is negligible. Experiments made with furfural in the presence of dilute sodium hydroxide, under conditions resembling those adopted for the synthesis of furylacrolein, which lasted dozens of hours, resulted in an extremely slight diminution of the alkali concentration. If we assume that a decrease in the quantity of alkali involves neutralizing the pyromucic acid, the amount of furfural used in this side reaction cannot be reflected in the outputs of furylacrolein.

Another possible reaction is bound up with the further condensation of the nascent furylacrolein with acetaldehyde, producing polyene compounds of the $C_4H_3O(CH{=}CH)_n{-}CHO$ type. It was found that this process plays a considerable part whenever an attempt is made to perform the reaction in a more highly concentrated solution, at a higher temperature, or with rapid addition of the acetaldehyde. In all these cases we always recovered, not a crystalline product, but a greasy one, distillation of which yielded more than 20% of higher condensation products.

We made it a point to check the possibility that aldol condensation products of the aldehydes were formed. If we assume that aldols are formed, it becomes clear that these condensation products differ from the products of crotonic

condensation by being more highly soluble in water. Once in solution, they may enter into further condensation, increasing the losses of furfural, on the one hand, and requiring a considerable overconsumption of acetaldehyde. We have experimentally proved the feasibility of an aldol condensation in accordance with the following equation:



In one of our experiments, we tried to synthesize furylpentadienal by condensing furylacrolein with acetaldehyde in an aqueous-alcoholic medium under conditions similar to those used for synthesizing the furylacrolein. The condensation product proved to be more soluble in water than the original furylacrolein, and only after acidification and gentle heating were we able to recover an oily product from the transparent solution which contained furylpentadienal and higher condensation products. Characteristically, if the mother liquor left after the furylacrolein is separated out is acidulated and heated, we also get a resinous product consisting of a mixture of polyene derivatives of furan. The more acetaldehyde is used, the more of this product is obtained. Thus, all reactions of the aldol type appreciably diminish the furylacrolein output and increase the consumption of acetaldehyde.

Lastly, it was found that the synthesis of furylacrolein is accompanied by the aldol condensation of acetaldehyde. The presence of aldol in the solution was proved after the furylacrolein had been separated out. When this solution is acidulated with sulfuric acid and then distilled, crotonaldehyde, formed from the aldol when it is heated in an acid medium, is found in the first runnings of the distillate. The lower the excess of acetaldehyde, the less aldol is formed.

The foregoing led us to the following conclusions: cutting down the formation of by-products requires that dilute solutions be used, with as low a concentration of acetaldehyde as possible; the rate at which the dilute solution of acetaldehyde is added should correspond to the rate of formation of the furylacrolein; the latter must be separated out of the solution as soon as it is formed, in order to hamper its entrance into side reactions of further condensation. These conclusions are borne out by our experiments. We tried to increase the output of furylacrolein while diminishing the excess of acetaldehyde below the quantity specified in Konig's procedure [1] by employing more highly diluted acetaldehyde and prolonging the time during which it is entered into the reaction.

Furylacrolein separates out as light-yellow crystals, with a m.p. of 48-50°, which quickly turn brown and are transformed into a blackish-brown mass when stored, especially in the light. These changes are due to the polymerization of the higher condensation products present as impurities. Even the furylacrolein that distills in vacuum within the range of one degree turns brown in storage, but much less so than the initial product. It is characteristic that the steam distillation of furylacrolein that has been kept for a long time yields white needles that are much more stable and undergo but little change in storage. This property may be due to the presence of a small amount of a readily changed geometrical stereo-isomer of furylacrolein.

Furylacrolein may be identified as its usual derivatives of aldehydes (m.p. of the oxime 123° [1]; of the phenylhydrazone 132° [1]; and of the semicarbazone 219° [2]). As our experiments have shown, furylacrolein reacts with sodium bisulfite, difficultly soluble crystals of a bisulfite derivative being first formed

in the cold; when gently heated, they can add another molecule of bisulfite at the double bond, thus forming the corresponding sulfo acid, which is recovered as its sodium salt only by cooling the reaction mass until it is well chilled.

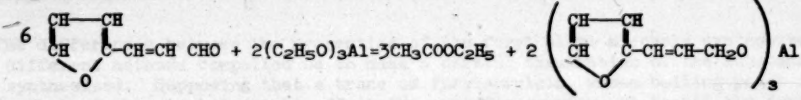
It is extremely noteworthy that furylacrolein, and its aqueous solution in particular, have an intensely sweet taste.

When acted upon by alkaline catalysts, furylacrolein can condense with aldehydes [1,2,4], ketones [5,6], and acid [7], giving rise to compounds with several double bonds. Furylacrolein, like the aromatic aldehydes, can react with amines [8] to form Schiff bases. In an acid medium or when bromine is present, polymethine or cyanine dyes can be secured from furylacrolein, depending on the reaction conditions.

A detailed study was made of the hydrogenation of furylacrolein with various catalysts [3,9]. Under severe hydrogenation conditions the furan ring ruptured, giving rise to heptane and heptanediol; with milder hydrogenation conditions, the hydrogen reduces the aldehyde group or else is added to the double bonds of the ring and the side chain. Bray and Adams [10] and their co-workers made a study of the selective hydrogenation of furylacrolein and asserted that in the presence of platinum and a trace of zinc and iron salts, with one mole of hydrogen absorbed, the reaction entails nothing but the reduction of the aldehyde group, without affecting the double bond. Thus, furyl allyl alcohol was synthesized for the first time as a colorless liquid, which thickens upon standing and yields naphthylurethane with a m.p. of 94°.

We resolved to make a more detailed study of this new alcohol, choosing the reduction of furylacrolein by aluminum ethylate as the method for its synthesis. Of late, the reduction of aldehydes and ketones with aluminum ethylate or isopropylate has become a method widely employed in organic synthesis, as it makes it possible to carry out the reduction under very mild conditions. We began with a series of experiments on the reduction of furylacrolein by aluminum ethylate under conditions that differed but little from the procedure employed for the reduction of other aldehydes. For example, reduction was carried out in the cold in a solution of absolute alcohol, with gentle heating, and with boiling, with and without passing a current of nitrogen through the mass. None of these experiments was very satisfactory, however: the output of furyl allyl alcohol did not exceed 20-30%; much of the furyl allyl alcohol polymerized to a thick, viscous mass or a solid tar. To prevent polymerization in subsequent experiments we used dilute benzene solution and a large excess of aluminum ethylate.

Under these conditions the output of furyl allyl alcohol rose to 60-70%. Experiments made to determine the quantity of acetaldehyde liberated in the reaction showed that, contrary to the assertions of numerous authors who have made a study of this process, only a very small amount of acetaldehyde is evolved under our conditions; the principal reaction product is ethyl acetate, which is formed in a Tishchenko reaction [12]. The reaction may be pictured by the following overall equation:



When toluene or xylene is used as the solvent and reduction is carried out at a temperature above 100°, the rate of distillation and the quantity of the distilled ethyl acetate prove that the synthesis of furyl allyl alcohol is completed

30 to 40 minutes after the solvent begins to boil.

The furyl allyl alcohol thus produced has a slightly yellowish tinge. Upon standing this color turns to yellow and then to red, and the substance changes into a transparent, extremely thick, viscous liquid. Approximately 50% of the alcohol polymerizes during the course of 3-4 months.

Furyl allyl alcohol is polymerized very violently by boron fluoride, sulfur dioxide, and tin, iron, and aluminum chlorides. When polymerized by boron fluoride at room temperature or with gentle heating, the furyl allyl alcohol turns black and, with the evolution of considerable heat, quickly turns into a brittle, lustrous resin, which is insoluble in organic solvents. When polymerization is effected with a weak ethereal solution of boron fluoride at temperatures below 0°, the process is slow, and the liquid turns dark-red, gradually thickens, loses its transparency, and changes within 6 to 7 days into an elastic mass. The polymerization of furyl allyl alcohol by sulfur dioxide is similar. When a few bubbles of sulfur dioxide are passed through the alcohol and it is set aside to stand at 5°, the very next day the alcohol changes into a viscous liquid that gradually loses its transparency and is transformed within the course of 8 to 10 days into a yellow orange mass possessing elastic properties. The mass grows darker when left to stand exposed to the air, becoming solid and losing its elasticity.

Contrary to the assertions of Bray and Adams [10], who state that the furyl allyl alcohol they synthesized does not form an ester when reacted with acetic anhydride, our product forms an acetate, with high yield, when reacted with acetic anhydride in the presence of anhydrous sodium acetate. It should be noted that we were unable to produce other esters, such as the oxalate, owing to the onset of polymerization of the furyl allyl alcohol. The alcohol we synthesized also differs considerably in its specific gravity.

The constants of the furyl allyl alcohol synthesized by various methods are compared in the following table:

Method of synthesizing furyl allyl alcohol	Boiling point	Sp. gr.	n_D	M.p of α-naphthyl-urethane
Selective hydrogenation of furylacrolein [10]	108-110° (4 mm)	$d_{20}^{20°}$ 1.1439	1.5520-27°	93-93.5°
Reduction of furylacrolein by aluminum ethylate.....	123-124° (20 mm)	$d_4^{17.5}$ 1.1001	1.5514-175	93-94
Refining the alcohol by heating it with silver oxide	118-120° (18 mm)	d_4^{18} 1.1050	1.5510-18°	-
Recovery via a molecular compound with $CaCl_2$.....	118-120° (18 mm)	d_4^{17} 1.1008	1.5494-17°	-
Furyl allyl acetate	127° (20 mm)	d_{28}^{28} 1.0987	1.5180-20°	-

The differences between the properties of the furyl allyl alcohols synthesized by two different methods compelled us to make a careful examination of the substance we had synthesized. Supposing that a trace of furylacrolein, whose boiling point is close to that of the alcohol, might affect the specific gravity, we heated the furyl allyl alcohol with an aqueous suspension of silver oxide; but this caused no noticeable changes in the constants. Adding up to 10% of furylacrolein to the furyl allyl alcohol increases the specific gravity somewhat, but this change is quite insignificant. Noting that our alcohol can form a molecular compound with calcium chloride,

we secured a certain amount of this compound, carefully washed it with ether, and decomposed it with water. The alcohol thus prepared had practically the same properties as the original product. The supposition that this difference in properties depends upon the existence of two cis-trans forms is not borne out by experiment, inasmuch as other constants, such as the refractive index and the melting point of α-naphthyl urethane, exhibit satisfactory agreement. What is most likely is that the American researchers [10] made a mistake in determining the specific gravity of furyl allyl alcohol, and this is indirectly confirmed by comparison of the constants of the hydrogenated derivatives of furyl allyl alcohol.

EXPERIMENTAL

Preparation of furylacrolein. 7 g of sodium hydroxide was dissolved in 1400 ml of water, and 100 g of freshly distilled furfural was added to the solution, chilled to 0°, during 10-15 minutes with constant stirring. 60 g of acetaldehyde in 300 ml of water was uniformly added to the resulting solution, at 0° and with constant stirring, from a dropping funnel during the course of 5 hours. As a rule, the acicular crystals of furylacrolein begin to settle out 40 to 50 minutes after the addition of the acetaldehyde is begun. If this does not take place, the addition of the acetaldehyde must be stopped, and the onset of crystallization must be initiated by rubbing with a glass rod or by introducing ready crystals of furylacrolein. Crystallization is usually delayed if the temperature of the reaction mixture has been allowed to rise above 0° or if the acetaldehyde has been added too rapidly. The furylacrolein then forms an emulsion, from which a greasy product is recovered as more acetaldehyde is added, which usually lowers the output of the pure furylacrolein. After all the acetaldehyde has been added, the reaction mixture is allowed to stand for 2 hours. The furylacrolein is drawn off, washed with chilled water, squeezed out on a press, and desiccated in the dark, either in an exsiccator or over calcium chloride. Neutralizing the filtrate with sulfuric acid and then steam-distilling it makes it possible to secure another 2 to 5 g of furylacrolein. The solubility of furylacrolein in water at 0° is about 2 g per liter. The yield ranges from 75 to 85%. It is advisable to recrystallize the product from aqueous alcohol or to distill it in vacuum or to distill it with steam, or, best of all, with slightly superheated steam, in order to secure pure furylacrolein.

Preparation of furyl allyl alcohol in alcoholic solution. Efforts to reduce the furylacrolein were made in the cold, with gentle heating, and by boiling. 10 g of pulverized aluminum ethylate was added to 20 g of furylacrolein in 15 ml of absolute alcohol. The flask was sealed with a stopper fitted with a calcium-chloride tube and allowed to stand 5 days at 20-25°.

The resulting thick brown mass was treated with 65 ml of 10% sulfuric acid and then extracted with ether. The residue after the ether had been driven off was distilled with steam. The distillate was extracted with ether, desiccated with sodium sulfate, and redistilled. This yielded 3.5 g of furyl allyl alcohol. Similar results were obtained by heating the reaction mass to 35-40°. It is worthy of note that when the acetaldehyde evolved was absorbed by powdered caustic alkali in U-shaped tubes connected in series to the reaction flask, only the aldehyde in the first tube resinifies, the gain in weight of this tube totaling only 0.2 g.

The output of furyl allyl alcohol rises somewhat, to 30-35%, when the reaction mass is heated to boiling and a gentle current of nitrogen is passed through it. The experiment was continued until the distillate no longer exhibited a positive reaction for acetaldehyde, which occurred after 15-18 hours.

Preparation of furyl allyl alcohol in a benzene solution. 60 g of furylacrolein, 300 ml of anhydrous benzene, and 50 g of coarsely ground aluminum ethylate were placed in a round-bottomed flask. The flask was sealed with a stopper fitted with a reflux condenser and a calcium-chloride tube and heated for 5 hours over a water bath. The solution turned dark brown, but no precipitate was formed, contrary to our experience in the preceding experiments. The benzene solution was poured into chilled 10% sulfuric acid in batches, with constant shaking, the amount of sulfuric acid being based on the assumption that all the aluminum is bound. After the aluminum alcoholate had been decomposed, there usually remained a small quantity of light-brown precipitate that was insoluble in benzene. The benzene layer was removed, and the aqueous one was again extracted twice, 50 ml being used each time. The combined benzene extracts were washed with a small amount of water and soda, and desiccated over calcined sodium sulfate. The benzene was driven off, and the residue (60 g) was distilled at 20 mm.

Fraction 1:	up to 117°	1.1 g
Fraction 2:	117-120°	1.3 g
Fraction 3:	120-124°	33.4 g
Fraction 4:	124-126°	6.1 g
Residue (a thick mass)		17.1 g.

Redistillation of the combined Fractions 3 and 4 yielded 28.7 g of furyl allyl alcohol:

B.p. 123-124° at 20 mm; $d_4^{17.5}$ 1.1001; $n_D^{17.5}$ 1.5514; MR_D 35.98.
$C_7H_8O_2$. Computed: MR_D 34.09.

The furyl allyl alcohol was identified by preparing α-naphthyl urethane by gently heating 3.4 g of α-naphthyl isocyanate with 2.5 g of furyl allyl alcohol. Upon cooling, the entire mass crystallized. The α-naphthyl urethane was purified by recrystallizing it from ligroin heated to 60°. Double recrystallization yielded minute acicular crystals with a m.p. of 93-94°.

0.1532 g substance: 4.85 ml 0.1N H_2SO_4.
Found %: N 4.43.
$C_{18}H_{15}O_3N$. Computed %: N 4.78.

Preparation of furyl allyl acetate. Furyl allyl alcohol was added to a 50% excess of acetaldehyde and 1.2 g of fused sodium acetate; the temperature of the mixture rose. The reaction was completed by heating the mixture over a water bath for 1 hour; the ester was washed with water and soda, desiccated with calcium chloride, and distilled in vacuum. Furyl allyl acetate is a colorless liquid with a pleasant odor:

B.p. 127°; d_{20}^{20} 1.0987; n_D^{20} 1.5180; MR_D 45.72.
$C_9H_{10}O_3$. Computed: MR_D 43.46.

The ester was analyzed by heating it with an alcoholic solution of caustic soda for one hour to saponify it.

0.830 g substance: 49.99 ml 0.1N solution NaOH.
Found %: CH_3CO 25.9.
$C_7H_7O_2(COCH_3)$. Computed %: CH_3CO 25.9.

Furylacrolein is reduced much more rapidly in a toluene solution. In one of our experiments we used 15 g of aluminum ethylate and 100 ml of anhydrous toluene for 20.3 g of furylacrolein. The reaction flask, fitted with a dephlegmator, was heated over an oil bath until the toleune boiled gently. The resulting ethyl acetate

was collected in a measuring cylinder. The bulk of the ethyl acetate, with a trace of acetaldehyde, distilled over within 25 minutes after the onset of boiling; the reaction was practically complete within 40 minutes.

Preparation of furyl allyl alcohol in a xylene solution without the formation of aluminum ethylate. The simplest way of synthesizing furyl allyl alcohol is as follows: 10-11 g of freshly prepared coarse aluminum powder, 100 ml of anhydrous xylene, and 1-2 g of previously prepared aluminum ethylate are placed in a round-bottomed flask fitted with a reflux condenser and a separating funnel. The flask is heated until the solvent boils, and 35 ml of absolute alcohol is added from a dropping funnel. Soon after the addition of the alcohol is begun, hydrogen begins to be evolved vigorously; the addition of more alcohol is so regulated as to prevent the reaction from becoming too violent. The mixture gradually turns into a thick, jellylike mass, and the reaction subsides considerably. To speed it up again, 100 ml of anhydrous xylene must be added; the mass is liquefied, and the evolution of hydrogen is increased considerably; toward the end of the reaction another 100 ml of xylene is added. Three to four hours later, when nearly all the aluminum has reacted, heating is stopped, and, after settling, the xylene solution of the aluminum ethylate is decanted while still hot together with the precipitate into a round-bottomed flask, 60 g of furylacrolein is added, and the whole is heated with a reflux condenser over a boiling water bath for 2.5 hours.

The mixture is gradually poured, with constant agitation and chilling, into 250 ml of 20% sulfuric acid. The precipitate, which sometimes forms during this treatment, is filtered out. It is useful to extract the aqueous layer once or twice with 30-40 ml of xylene, and the combined extracts are desiccated with calcined potash or sodium sulfate. The xylene is driven off in a slight vacuum over a water bath, it being well to add a little hydroquinone or pyrogallol to prevent polymerization of the furyl allyl alcohol. The residue left after the solvent has been driven off is distilled in vacuum (20 mm) at 122-124°. The output of furyl allyl alcohol is 60-70%. The product yield may be raised considerably by lessening the polymerization of the furyl allyl alcohol during synthesis and purification.

SUMMARY

1. The procedure for preparing furylacrolein has been refined, and the side reactions that lessen its output have been explored. It has been found that aqueous solutions of furylacrolein possess an intensely sweet taste.

2. The reduction of furylacrolein to furyl allyl alcohol by aluminum ethylate has been studied. It has been established that reduction is rapid in solutions of aromatic hydrocarbons, the acetaldehyde that is formed being converted into ethyl acetate in a Tishchenko reaction.

3. The constants of furyl allyl alcohol have been defined more accurately, and its acetate has been synthesized for the first time.

4. It has been established that furyl allyl alcohol polymerizes readily, giving rise to solid, brittle resins, thick, viscous oils, or a mass with marked elastic properties.

LITERATURE CITED

[1] Konig, Hey, Ber., 58, 2563 (1925).

[2] Ivanov, Bl. Soc. chim., (4), 35, 1658 (1924).

[3] Hinz, Meyer, Schucking, Ber., 76, 676 (1943).

[4] Schmitt, Lieb Ann., 547, 270 (1941).

[5] Rutchenko, J. Gen. Chem., 10, 1953 (1940).

[6] Maxim, Popescu, Bul. Soc. chim., (5), 5, 49 (1938).

[7] Rohmer, Ber., 31, 281 (1898); Z.phys. Chem., 29, 378 (1935).

[8] Rutchenko, Sci. Notes Kazan Univ., 100 (1940); Konig, Ber., 67, 1274 (1934).

[9] Orlov, Glinskikh, and Ignatovich, J. Appl. Chem., 8, 1170 (1935); J. Am. Chem. Soc., 56, 438 (1934); Zbl., 1930, I, 224.

[10] Bray, Adams, J. Am. Chem.Soc. 49, 2101 (1927).

[11] Neuere Methoden der Praparativen Organischen Chemie. Verlag Chemie, 1943, page 137; Organic Reactions, 11, page 178, New York, 1942.

[12] Tishchenko, J. Russ. Chem. Soc., 38, 355 (1906).

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RESEARCH IN THE FIELD OF FURAN DERIVATIVES

II. SYNTHESIS AND PROPERTIES OF THE ESTERS OF γ-KETOPIMELIC ACID

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The cleavage of the furan ring by hydrogen chloride, giving rise to γ-keto acids, has been observed by many authors for such α-substituted furan derivatives as contain either a hydroxyl group or a double bond in the side chain at the carbon directly attached to the furan ring. Furyl alcohol or its homologs are transformed by this treatment into laevulinic acid or the latter's ω-substituted derivatives.

Both monobasic [2] and dibasic acids [3] are secured by cleaving compounds possessing double bonds. By heating furylacrylic acid in alcoholic solution with concentrated hydrochloric acid, Marckwald [4] was the first man to synthesize γ-ketopimelic acid and its diethyl ester, with varying yields. Volhard [5] made a more thorough study of this reaction, but he was unable to make any essential improvement in the procedure for synthesizing this acid. Only comparatively recently has a procedure been put forward that makes it possible to secure diethyl γ-ketopimelate with a nearly theoretical yield [6]. In this method, a current of gaseous hydrogen was passed through a heated solution of furylacrylic acid in absolute ethyl alcohol, after which the reaction mixture was heated for two hours. A deficiency of the procedure described was the lack of precise information on the temperature of the process and on the time during which the hydrogen chloride was passed through, which is of some importance, as our tests demonstrated.

Of the esters of γ-ketopimelic acid, only the dimethyl ester, produced by the esterification of the free acid [5], and the diethyl ester, prepared from furylacrylic acid [4,6], have been described.

In a desire to learn whether the nature of the alcohol affects the process of forming the γ-ketopimelic acid, we conducted experiments with furylacrylic acid dissolved in primary alcohols, beginning with methyl and ending with isoamyl alcohol. The reaction is independent of the alcohol's molecular weight, proceeding with equal ease and forming the respective esters of γ-ketopimelic acid. It was found that the furylacrylic acid is first esterified. As more hydrogen chloride is passed through the mixture, the esters that form are converted, with a slight rise in temperature, into esters of γ-ketopimelic acid. In all the experiments in which

little hydrogen chloride was passed through or the temperature of the reaction medium was allowed to drop, large quantities of undecomposed esters of furylacrylic acid were left over.

All the synthesized esters of γ-ketopimelic acid are colorless, mobile liquids with a faint odor. When kept for a long time they turn slightly yellow. The esters of γ-ketopimelic acid form phenylhydrazones with great ease; these are slightly yellowish crystalline products, which turn an intense yellow within a few hours after their formation and are converted into dark-red oily products. The principal constants of the esters of γ-ketopimelic acid synthesized by us are listed in the subjoined table.

Ester of γ-ketopimelic acid	Formula	Boiling point at 20 mm	d_{20}^{20}	n_D^{20}	MR_D found	MR_D computed	Melting point of the phenylhydrazone.
Dimethyl ...	$C_9H_{14}O_5$	m.p. 54°	–	–	–	–	84°
Diethyl	$C_{11}H_{18}O_5$	182°	1.0855	1.4432	56.21	56.32	63
Dipropyl ...	$C_{13}H_{22}O_5$	201	1.0441	1.4442	65.66	65.55	50
Dibutyl.....	$C_{15}H_{26}O_5$	216	1.0179	1.4448	74.76	74.79	53
Diisobutyl..	$C_{15}H_{26}O_5$	203	1.0090	1.4420	75.01	74.79	66.5
Diisoamyl ...	$C_{17}H_{30}O_5$	221.5	0.9966	1.4462	84.05	84.02	53.5

EXPERIMENTAL

Synthesis of dipropyl γ-ketopimelate. 13.8 g (0.1 mol) of furylacrylic acid, with a m.p. of 140-141°, was placed in a small round-bottomed flask and dissolved by heating it in 35 g of n-propyl alcohol. A current of hydrogen chloride, prepared with 13.0 g of ammonium chloride, was passed through the solution at 70° for 30 minutes. At first the temperature dropped several degrees, and then it began to rise slowly, reaching 87° 15 minutes after we began to pass the hydrogen chloride through, after which it began to fall slowly. The solution gradually turned red, and then turned dark-brown. The reaction mixture was heated to a gentle boil for two hours with a reflux condenser. The excess alcohol was driven off, a small quantity of propyl chloride being found in the 50-90° fraction. The residue was washed with cold water to which anhydrous soda had been added until no more carbon dioxide was evolved, then desiccated with calcium chloride, and distilled in a 20-mm vacuum. The bulk of the residue, 22.4 g, distilled over at 198-203°. Upon redistillation we collected a principal fraction with a b.p. of 201°. A colorless liquid with a slight agreeable odor.

The synthesized ester was analyzed by saponifying it with an alcoholic solution of titrated sodium hydroxide. 1.1115 g of the ester was heated to boiling with a reflux condenser for one hour with 50 ml of ethyl alcohol and 20.8 ml of NaOH (T = 0.03626). The liquid was diluted with water to a volume of 500 ml and titrated several times with 50 ml of 0.1N hydrochloric acid and phenolphthalein. A blank test was run at the same time. Saponification of all the ester required 0.3437 g of NaOH, which corresponds to a content of 99.69% of dipropyl γ-ketopimelate.

The phenylhydrazone was prepared as follows: 1.29 g of the dipropyl γ-ketopimelate was dissolved in 15 ml of 80% acetic acid, and then 0.8 g each of phenyl-

hydrazine hydrochloride and sodium acetate were added. The mixture was heated for 20 minutes and cooled in a freezing mixture, after which about 1 ml of water was added drop by drop until a copious precipitate settled out. The precipitate was filtered out, washed with water, and recrystallized from 8 ml of ethyl alcohol diluted with 2 ml of water.

The phenylhydrazone of dipropyl γ-ketopimelate consists of yellowish, acicular crystals with a m.p. of 50°. The substance decomposes in storage, so that all the operations required in producing the phenylhydrazone must be performed quickly.

Synthesis of dibutyl γ-ketopimelate. 27.6 g (0.2 mol) of furylacrylic acid was dissolved in 80 ml of n-butyl alcohol and a current of hydrogen chloride was passed through for 30 minutes at 70°. The HCl was produced from 15 g of ammonium chloride instead of the 26 g used in the preceding experiment. Fractionation in vacuum (20 mm) yielded two fractions: 12 g of Fraction 1 distilled at 160-200°, and 23 g of Fraction 2 distilled at 215-280°.

Fraction 1 proved to be a mixture consisting of butyl furylacrylate and dibutyl γ-ketopimelate. The butyl furylacrylate formed during the first phase could not be converted into the end product – dibutyl γ-ketopimelate – because of an insufficiency of hydrogen passed through the reaction mixture.

Fraction 2 was redistilled, 15 g of a principal fraction, boiling at 216° and 20 mm, being collected. The principal constants of the ester are listed in the table. Saponification of the ester required 0.2871 g of NaOH, which corresponds to a content of 99.73% of dibutyl γ-ketopimelate. The phenylhydrazone, prepared from 0.7 g of the ester, was recrystallized from slightly diluted alcohol and melted at 53.0°.

Synthesis of diisobutyl γ-ketopimelate. We used 13.8 g of furylacrylic acid and 45 g of isobutyl alcohol. The experimental procedure was like that used in the synthesis of the dipropyl ester. No fraction corresponding to isobutyl furylacrylate was recovered. Double distillation at 20 mm yielded 13.1 g of a fraction that boiled at 203° (constants listed in the table). Saponification of 1.0230 g of the ester required 0.2856 g of NaOH, which corresponds to a content of 99.82% of diisobutyl -ketopimelate. The phenylhydrazone fuses at 66.5°.

Synthesis of diisoamyl γ-ketopimelate. Passing the hydrogen chloride evolved from 10 g of ammonium chloride through 13.8 g (0.1 mol) of furylacrylic acid and 52 g of isoamyl alcohol yielded 8.6 g of a fraction that boiled at 161-173° and 20 mm, and 11.9 g of a fraction that boiled at 220-224° and 20 mm. Refractionation of Fraction 1 yielded a substance that passed over almost completely at 161.5-162.5° and 20 mm as a colorless, mobile liquid with a pleasant odor, which turns yellow fairly quickly when exposed to light, however: d_{20}^{20} 1.0229; d_4^{20} 1.0215; n_D^{20} 1.5221.

Saponification of this liquid yielded isoamyl alcohol and furylacrylic acid with a m.p. of 139°, which exhibited no depression when mixed with a test sample of pure furylacrylic acid. This indicated that the substance synthesized was isoamyl furylacrylate, which was produced in the given experiment because of an insufficiency of hydrogen chloride and shorter heating of the reaction mixture.

Refractionation of Fraction 2 yielded 9.6 g of pure diisoamyl γ-ketopimelate, with a m.p. of 221.5° at 20 mm; d_4^{20} 0.9952 (the other constants are listed in the table.)

Saponification of 1.2006 g of the ester required 0.3059 g of NaOH, which corresponds to a content of 99.36% of diisoamyl γ-ketopimelate. The phenylhydrazone

consists of nearly colorless crystals with a m.p. of 53.5°.

Synthesis of dimethyl γ-ketopimelate. The dimethyl ester was initially synthesized from the ready γ-ketopimelic acid and methanol [5]. We endeavored to synthesize it from furylacrylic acid dissolved in methanol. After hydrogen chloride had been passed through the heated dark-brown solution, a copious crystalline precipitate was thrown down when the solution cooled. When this precipitate was treated with a soda solution until its reaction was neutral, part of it passed into the aqueous layer, from which the free γ-ketopimelic acid was recovered by acidulation with sulfuric acid. Recrystallization from water yielded snow-white, lustrous crystals with a pleasant sweet taste and a m.p. of 142°. A test sample mixed with furylacrylic acid exhibited a marked depression; the m.p. of the mixture was 121.5°.

The acid was analyzed by titration with NaOH in the presence of phenolphthalein. Neutralization of 0.0980 g of acid required 0.0451 g of NaOH, which corresponds to a content of 99.96% of γ-ketopimelic acid. The residue left after treatment with soda was recrystallized from methanol and then from petroleum ether. The substance recovered, with a m.p. of 54°, is dimethyl γ-ketopimelate. The phenylhydrazone, produced by the method described above, consists of nearly white crystals with a m.p. of 84°.

Synthesis of diethyl γ-ketopimelate. Contrary to the procedure previously described [4,6], we synthesized this ester by reacting pure ethyl furylacrylate with hydrogen chloride. 22.5 g of ethyl furylacrylate, dissolved in 30 ml of (97.5%) alcohol yielded 16.1 g of diethyl γ-ketopimelate after hydrogen chloride (prepared from 20 g of ammonium chloride) had been passed through the solution heated to 65°. Refractionation of the ester caused it to distil at 182° and 20 mm (see the table for the other constants).

Saponification of 1.1031 g of the ester required 0.3832 g of NaOH, which corresponds to a content of 99.88% of diethyl γ-ketopimelate. The phenylhydrazone, prepared from 2.3 g of the ester, 1.8 g of the phenylhydrazine hydrochloride, and 1.8 g of CH_3COONa in 15 ml of 80% acetic acid, had a m.p. of 63° after recrystallization from alcohol.

Like γ-ketopimelic acid, which forms a normal phenylhydrazone according to the references in the literature, all the esters of this acid also form hydrazones very readily. These latter change in structure upon standing, being converted, apparently, into heterocyclic compounds. The analysis [7] of the synthesized phenylhydrazone was performed by the Kjeldahl method, the weighed portion being reduced with zinc dust before combustion.

0.1678 g substance: 10.67 ml 0.1N solution H_2SO_4.
0.1680 g substance: 10.25 ml 0.1N solution H_2SO_4.
Found %: N 8.90, 8.54.
$C_{17}H_{24}O_4N_2$. Computed %: N 8.75.

SUMMARY

1. The dimethyl, diethyl, dipropyl, dibutyl, diisobutyl, and diisoamyl esters of γ-ketopimelic acid have been synthesized from furylacrylic acid by using hydrogen chloride to rupture the furan ring, and their phenylhydrazones have been prepared.

2. It has been found that during the first stage of this reaction esters of furylacrylic acid are formed, which are later converted by the hydrogen chloride into esters of γ-ketopimelic acid. When the amount of hydrogen chloride

present is insufficient, a mixture of these esters is produced, and when a considerable excess of the hydrogen chloride is present, an appreciable quantity of tarry substances is produced.

LITERATURE CITED

[1] Berkenheim and Dankova, J. Gen. Chem., 9, 824 (1939); Ushakov and Kucherov, J.Gen.Chem., 14, 1073 (1944).

[2] Kehrer, Igler, Ber., 32, 1176; 34, 1263; Thiele, Landers, Lieb. Ann, 362 300.

[3] Kehrer, Hofacker, Lieb. Ann., 294, 165.

[4] Marckwald, Ber., 10, 357; 21, 1398.

[5] Volhard, Lieb. Ann., 253, 235.

[6] Chichibabin, Chim. et Ind., 27, 563.

[7] Meyer. The Analysis and the Determination of the Structure of Organic Compounds, p. 406.

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C-ALKYL-SUBSTITUTED MORPHOLINES

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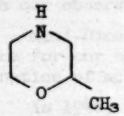
The literature on the synthesis of morpholine and its N-alkyl and N-aryl derivatives is extraordinarily extensive; but there are but few papers on the synthesis of C-alkyl-substituted morpholines [1,2,3,4,5].

One of the most satisfactory methods of synthesizing the C-substituted morpholines is, no doubt, the cyclization of dialkanolamines by means of various dehydrating agents [3]. Krasusky [4] cyclized diisopropanolamine in the presence of 70% sulfuric acid, securing a yield of 22% of 2,6-dimethylmorpholine.

The present paper describes the synthesis of the following mono- and dialkyl-substituted morpholines: 2-methylmorpholine (I); 3-methylmorpholine (II); 2,5-dimethylmorpholine (III); 3,5-dimethylmorpholine (IV); 2-ethylmorpholine (V); 2-ethyl-5-methylmorpholine (VI); and 2,6-diethylmorpholine (VII):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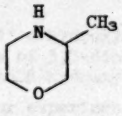
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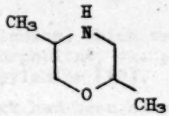
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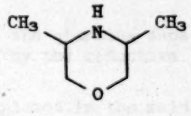
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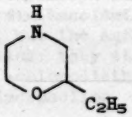
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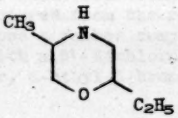
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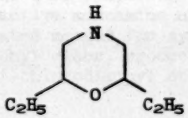
(VII)

All of these compounds were synthesized by dehydrating the corresponding dialkanolamines by the method developed by Medard [6] for the synthesis of morpholine, i.e., by heating to 175-180° with 95-98% sulfuric acid for 8 hours.

The isolation of morpholines in the free state is accompanied by fairly high

losses, as these substances are very hydrophilic and hygroscopic (with the exception of 2,6-diethylmorpholine, which is insoluble in water). The last traces of moisture were eliminated by prolonged desiccation over fused alkali and distillation above metallic sodium. In the light of the foregoing, the morpholine yield was computed in terms of their hydrochlorides, dried in a vacuum exsiccator to constant weight; it averaged 80-85% of the theoretical.

The C-alkyl-substituted morpholines were identified by their well-crystallizing phenylthiourea derivatives, which may be produced fairly easily by reacting them with a concentrated alcoholic solution of phenyl isothiocyanate.

Morpholine	M.p. of the phenylthiourea derivative
2-Methylmorpholine	136.5-137°
3-Methylmorpholine	121.5-122.5
2,6-Dimethylmorpholine	137-138.5
2,5-Dimethylmorpholine	145-147
3,5-Dimethylmorpholine	122-123
2-Ethylmorpholine	126-127
2-Ethyl-5-methylmorpholine	117-119
2,6-Diethylmorpholine	106-107

Nearly all the dialkanolamines that served as the raw materials in the synthesis of these compounds were prepared by condensing the respective monoalkanolamines or ammonia with olefin oxides and were identified by their picrates. In contrast to the conditions employed for similar reactions by Knorr [7] and Krasusky [8], who used aqueous solutions of the bases, we used oxyamines in both 95% and absolute alcohol, achieving satisfactory results in both cases. The latter circumstance does not agree with the statements of Knorr and Krasusky that water must be present for this reaction to follow its normal course. On the other hand, Horne and Shriner [9], in their study of the reaction of ethylene oxide with diethylamine, assert that this reaction takes place in absolute methanol or ethyl alcohol as well as in water, which is in agreement with our observations.

α,α'-Dimethyl-β,β'-dihydroxydiethylamine, which served as the starting substance for our synthesis of 3,5-dimethylmorpholine, was produced by the reductive amination of acetol with β-hydroxyisopropylamine [10].

In 1946, after our experimental work had been already completed in the main, Cottle and his co-workers [11] published a paper in which they report the synthesis of 2-methylmorpholine, 3,3-dimethylmorpholine, 3-ethylmorpholine, 2-methyl-5-ethyl-morpholine, and 2-ethylmorpholine. The first four compounds were synthesized by dehydrating the dialkanolamines, prepared from the respective monoamino alcohols and olefin oxides, but the authors chose a rather complicated method for synthesizing 2-ethylmorpholine: they started with α,β'-dichlorodiethyl ether, proceeding via α,β-dibromo-β-chlorodiethyl ether, α-ethyl-β-bromo-β'-chlorodiethyl ether, and 2-ethyl-4-phenylmorpholine.

In our opinion this procedure is unjustified, inasmuch as it would be simpler to synthesize 2-ethylmorpholine from butylene oxide and monoethanolamine, i.e., by the same method the authors used to synthesize the other C-alkyl-substituted morpholines.

Unfortunately, the authors did not confirm the non-identity of the isomeric morpholines by comparing the constants of their crystalline derivatives.

EXPERIMENTAL

2-Methylmorpholine (I)

a) β-Methyl-β,β'-dihydroxydiethylamine. A mixture of 80 g of freshly distilled monoethanolamine and 100 g of ethyl alcohol was placed in a three-necked flask fitted with a stirrer, a dropping funnel, and a thermometer. Then, a solution of 15 g of propylene oxide in 15 ml of alcohol was added drop by drop, with chilling and constant stirring. The temperature of the reaction mixture was kept between 0 and +5°. After the alcohol and the excess monoethanolamine had been eliminated, the residue was double distilled in vacuum. The output of the dialkanolamine was 20 g (66% of the theoretical).

B.p. 135° at 10 mm; n_D^{17} 1.4695; d_4^{17} 1.0442; MR_D 31.77.
$C_5H_{13}O_2N$. Computed: MR_D 31.91.

4.101 mg substance: 7.552 mg CO_2; 4.004 mg H_2O.
0.1711 g substance: 14.2 ml 0.1N HCl (titration)
Found %: C 50.22; H 10.93; N 11.61.
$C_5H_{13}O_2N$. Computed %: C 50.42; H 10.92; N 11.76.

The picrate was prepared from a saturated solution of picric acid in absolute ether; it was recrystallized from a mixture of benzene and alcohol. Yellow prisms, with a m.p. of 120.5-121°, highly soluble in alcohol, water, and acetone, and insoluble in ether and benzene.

3.555 mg substance: 0.500 ml N_2 (14°, 739 mm).
Found %: N 16.25.
$C_{11}H_{16}O_9N_4$. Computed %: N 16.09.

b) 2-Methylmorpholine. 12 ml (22 g) of H_2SO_4 (sp. gr. 1.84) was carefully added, with chilling and constant stirring, to 14.4 g of β-methyl-β,β'-dihydroxydiethylamine. The mixture was heated over an oil bath in a round-bottomed flask fitted with a thermometer and an air-cooled reflux condenser. Heating was continued for 8 hours with the temperature within the flask kept at 170-180°; the mixture was partially carbonized, turning dark and foaming rather strongly. After it had been cooled, the reaction product was carefully alkalinized with a solution of 25 g of KOH in 150 ml of water. The voluminous precipitate of potassium sulfate that settled out was filtered out, and the alcohol, water, and methylmorpholine were distilled from the filtrate. When two-thirds of the liquid had been distilled, more water was added to the flask, and distillation was resumed. This operation was repeated three times. The distillates were acidified with 0.1N HCl until the reaction to Congo was acid and then evaporated in vacuum over a water bath to dryness. The residue was methylmorpholine hydrochloride in the shape of a crystallizable, slightly yellowish, highly hygroscopic mass.

After desiccation, the hydrochloride was mixed with 15 g of finely pulverized potassium hydroxide, and the resulting base was fractionated. A 130-136° fraction was collected. It weighed 9.3 g (80% of the theoretical). After being twice desiccated over fused caustic potash, the 2-methylmorpholine was redistilled. A colorless liquid with the characteristic sharp odor of an amine.

B.p. 134-136°; n_D^{17} 1.4490; d_4^{17} 0.9581; MR_D 28.27.
$C_5H_{11}ON$. Computed: MR_D 28.33.

4.155 mg substance: 0.485 ml N_2 (9°, 743 mm)
Found %: N 13.77.
$C_5H_{11}ON$. Computed %: N 13.85.

The phenylthiourea derivative was produced by mixing alcoholic solutions of 2-methylmorpholine and phenyl isothiocyanate. Thin, colorless lamellae, which dissolve with difficulty in water, but are readily soluble in alcohol and ether. M.p. 146.5-147° (from water).

4.755 mg substance: 0.490 ml N_2 (14.5°, 741 mm).
Found %: N 11.90.
$C_{12}H_{16}ON_2S$. Computed %: N 11.86.

3-Methylmorpholine (II)

a) α-Methyl-β,β'-dihydroxydiethylamine. A highly chilled solution of 1.5 g of distilled ethylene oxide in 10 ml of absolute ethyl alcohol was slowly added, with chilling and constant stirring, to a solution of 5 g of β-hydroxyisopropylamine, prepared by reducing acetol oxime [12], in 50 ml of absolute ethyl alcohol. After the solvent and the excess of the β-hydroxyisopropylamine had been driven off, the residue was distilled in vacuum. This yielded 3.8 g (95% of the theoretical) of the dialkanolamine with a b.p. of 151-152° at 15 mm. A slightly yellowish, viscous liquid, which is readily soluble in water and alcohol, but is insoluble in ether.

n_D^{16} 1.4707; d_4^{16} 1.0667; MR_D 31.16.

$C_5H_{13}O_2N$. Computed: MR_D 31.91.

0.0755 g substance: 6.22 ml 0.1N HCl (titration).
Found %: N 11.53.
$C_5H_{13}O_2N$. Computed %: N 11.76.

Picrate - consisted of long thin crystals, colored yellow. The m.p. was 101.5-102° after recrystallization from a mixture of ethyl acetate and absolute alcohol.

2.390 mg substance: 0.343 ml N_2 (20°, 735 mm)
Found %: N 16.12.
$C_{11}H_{16}O_9N_4$. Computed %: N 16.09.

b) 3-Methylmorpholine. A mixture of 2.8 g of α-methyl-β,β'-dihydroxydiethylamine and 4.3 g of H_2SO_4 (sp. gr. 1.84) was heated for 8 hours to 170-180°. The reaction product was treated in the same way as that used for 2-methylmorpholine. The 3-methylmorpholine hydrochloride weighed 3 g (93% of the theoretical). A solution of 5 g of caustic soda in 30 ml of water was added to the resulting hydrochloride. The oil that separated out was extracted with ether; the ethereal solution was twice desiccated with fused KOH; after the ether had been driven off, the residue was distilled over metallic sodium. The recovered base had a b.p. of 133-134°.

n_D^{16} 1.4517; d_4^{16} 0.9591; MR_D 28.39.

$C_5H_{11}ON$. Computed: MR_D 28.33.

0.0642 g substance: 6.20 ml 0.1N HCl (titration).
Found %: N 13.52.
$C_5H_{11}ON$. Computed %: N 13.85.

Phenylthiourea derivative - colorless needles (from aqueous alcohol) with a m.p. of 121.5-122.5°.

6.179 mg substance: 5.15 ml 0.01N H_2SO_4 (Kjeldahl)
Found %: N 11.67.
$C_{12}H_{16}N_2OS$. Computed %: N 11.86.

2,5-Dimethylmorpholine (III)

a) α,β'-Dimethyl-β,β'-dihydroxyethylamine. 3 g of propylene oxide in 10 ml of absolute methanol was slowly added, with stirring, to a chilled solution of 6 g of β-hydroxyisopropylamine in 50 ml of absolute methanol. After the solvent and the excess hydroxyamine had been eliminated, the residue was distilled in vacuum. This yielded 5.2 g of the substance (76% of the theoretical).

B.p. 140° at 12 mm; n_D^{16} 1.4609; d_4^{16} 1.0129; MR_D 36.03.
$C_6H_{15}O_2N$. Computed: MR_D 36.53.

5.330 mg substance: 0.480 ml N_2 (17°, 744 mm).
Found %: N 10.26.
$C_6H_{15}O_2N$. Computed %: N 10.52.

b) 2,5-Dimethylmorpholine. A mixture of 4 g of α,β'-dimethyl-β,β'-dihydroxydiethylamine and 5.5 g of H_2SO_4 (sp. gr. 1.84) was heated for 8 hours over an oil bath to 170-180°. The reaction product was then treated as in the preceding experiments. The base recovered after alkaline treatment was extracted with ether; after desiccation and after the solvent had been driven off, the residue was distilled over metallic sodium.

B.p. 145°; n_D^{16} 1.4459; d_4^{16} 0.9362; MR_D 32.76.
$C_6H_{13}ON$. Computed: MR_D 32.95.

6.960 mg substance: 6.00 ml 0.1 N H_2SO_4 (Kjeldahl).
Found %: N 12.07.
$C_6H_{13}ON$. Computed %: N 12.17.

Phenylthiourea derivative – thick, colorless prisms with a m.p. of 145-147° (from 50% alcohol).

4.697 mg substance: 0.485 ml N_2 (17.5°, 721 mm).
Found %: N 11.51.
$C_{13}H_{18}ON_2S$. Computed %: N 11.20.

3,5-Dimethylmorpholine (IV)

10.4 g of concentrated sulfuric acid (sp. gr. 1.84) was added to 7.5 g of α,α'-dimethyl-β,β'-dihydroxydiethylamine, produced by the reductive amination of acetol with β-hydroxyisopropylamine [10]. The mixture was heated to 170-180° for 8 hours and then treated as in the preceding experiments. The dimethylmorpholine hydrochloride weighed 7.9 g (94% of the theoretical). The base recovered after alkalinization was distilled over metallic sodium.

B.p. 142.5°; n_D^{16} 1.4460; d_4^{16} 0.9308; MR_D 32.95.
$C_6H_{13}ON$. Computed: MR_D 32.95.

0.1633 g substance: 13.98 ml 0.1N HCl (titration)
Found %: N 11.98.
$C_6H_{13}ON$. Computed %: N 12.17.

Phenylthiourea derivative – colorless needles with a m.p. of 122-123° (from methanol).

8.281 mg substance: 6.66 ml 0.01 N H_2SO_4 (Kjeldahl).
Found %: N 11.26.
$C_{13}H_{18}ON_2S$. Computed %: N 11.20.

2-Ethylmorpholine (V)

a) β-Ethyl-β,β'-dihydroxydiethylamine. A solution of 4 g of α-butylene oxide

in 15 ml of absolute ethyl alcohol was gradually added, with chilling and stirring, to a solution of 10 g of monoethanolamine in 50 ml of absolute ethyl alcohol. After the solvent had been driven off, the residue was fractionated in vacuum. This yielded 4.5 g (61% of the theoretical) of the dialkanolamine, with a b.p. of 137° at 9 mm.

n_D^{18} 1.4651; d_4^{18} 1.0115; MR_D 36.36.
$C_6H_{15}O_2N$. Computed: MR_D 36.58.

4.277 mg substance: 0.379 ml N_2 (10.5°, 735.5 mm).
Found %: N 10.32.
$C_6H_{15}O_2N$. Computed %: N 10.52.

b) 2-Ethylmorpholine. A mixture of 7.2 g of β-ethyl-β,β'-dihydroxydiethylamine and 10 g of concentrated sulfuric acid (sp. gr. 1.84) was heated to 170-180° for 8 hours. The reaction product was treated as in the preceding experiments. The ethylmorpholine hydrochloride weighed 4.2 g. The yield was 51% of the theoretical. The base produced was distilled over metallic sodium.

B.p. 141°; n_D^{20} 1.4499; d_4^{20} 0.9527; MR_D 32.43.
$C_6H_{13}ON$. Computed: MR_D 32.95.

0.0568 g substance: 4.90 ml 0.1N HCl (titration).
Found %: N 11.91.
$C_6H_{13}ON$. Computed %: N 12.17.

Phenylthiourea derivative – minute tetragonal tablets with a m.p. of 126-127° (from absolute alcohol).

3.530 mg substance: 0.335 ml N_2 (13.5°, 752 mm).
Found %: N 11.19.
$C_{13}H_{18}ON_2S$. Computed %: N 11.20.

2-Ethyl-5-methylmorpholine (VI)

a) α-Methyl-β'-ethyl-β,β'-dihydroxydiethylamine. A solution of 5 g of α-butylene oxide in 15 ml of alcohol was added, with stirring, to a chilled solution of 10 g β-hydroxyisopropylamine in 50 ml of alcohol. After the solvent had been driven off, the residue was distilled in vacuum. This yielded 6.7 g of an extremely viscous yellowish liquid with a b.p. of 134-136° at 8 mm. The substance crystallized as thin, irregular platelets after 2 days had elapsed. The m.p. of the dialkanolamine was 76.6-79°, after recrystallization from absolute alcohol. The yield was 65% of the theoretical.

0.2206 g substance: 14.8 ml 0.1N HCl (titration).
Found %: N 9.40.
$C_7H_{17}O_2N$. Computed %: N 9.52.

The picrate consisted of short yellow tetragonal prisms, with a m.p. of 115-116.5° (from an alcohol-ether mixture).

7.721 mg substance: 8.12 ml 0.01 N H_2SO_4 (Kjeldahl).
Found %: N 14.72.
$C_{13}H_{20}O_9N_4$. Computed %: N 14.89.

b) 2-Ethyl-5-methylmorpholine. A mixture of 5 g of α-methyl-β'-ethyl-β,β'-dihydroxydiethylamine and 6.5 g of concentrated sulfuric acid (sp. gr. 1.84) was heated to 170-180° for 8 hours. Treatment of the reaction product yielded 5.3 g of 2-ethyl-5-methylmorpholine hydrochloride (yield = 94.6% of the theoretical), from which the base was produced as a colorless liquid with a b.p. of 162-164°.

n_D^{18} 1.4480; d_4^{18} 0.9231; MR_D 37.41.
$C_7H_{15}ON$. Computed: MR_D 37.90.

0.0910 g substance: 6.95 ml 0.1N HCl (titration).
Found %: N 10.70.
$C_7H_{15}ON$. Computed %: N 10.85.

Phenylthiourea derivative – long, thin, platelets with a m.p. of 117-119° (from aqueous alcohol).

7.035 mg substance: 5.20 ml 0.01 N H_2SO_4 (Kjeldahl).
Found %: N 10.35.
$C_{14}H_{20}ON_2S$. Computed %: N 10.6.

2,6-Diethylmorpholine (VII)

a) β,β'-Diethyl-β,β'-dihydroxydiethylamine. 13 g (0.2 mol) of chilled α-butylene oxide was gradually added, with chilling and stirring, to a saturated solution of ammonia [15 g (0.9 mol)] in absolute ethyl alcohol. The residue left after the alcohol and the excess ammonia had been driven off was distilled in vacuum. A fraction with a b.p. of 145-146° at 13 mm was collected as a viscous liquid, which quickly crystallized upon standing. The substance had a m.p. of 79.5-80.5° after recrystalization from ether.

3.940 mg substance: 0.297 ml N_2 (16.5°, 745 mm).
Found %: N 8.70.
$C_8H_{19}O_2N$. Computed %: N 8.69.

The picrate consisted of thin, dendritic yellow needles with a m.p. of 145-147° (from alcohol).

2.637 mg substance: 0.336 ml N_2 (21.5°, 745 mm).
Found %: N 14.41.
$C_{14}H_{22}O_9N_4$. Computed %: N 14.35.

b) 2,6-Diethylmorpholine. A mixture of 11 g of β,β'-diethyl-β,β'-dihydroxydiethylamine and 12 g of concentrated sulfuric acid was heated to 170-180° for 8 hours. After the usual treatment, we secured 9.1 g of the diethylmorpholine (yield = 70% of the theoretical). The base produced from the latter by alkalinization was a mobile liquid with a b.p. of 178-179°, which is insoluble in water.

n_D^{18} 1.4550; d_4^{18} 0.9175; MR_D 42.29.
$C_8H_{17}ON$. Computed: MR_D 42.52.

3.942 mg substance: 0.341 ml N_2 (22°, 743 ml).
Found %: N 9.78.
$C_8H_{17}ON$. Computed %: N 9.79.

Phenylthiourea derivative – long hexagonal platelets with a m.p. of 106-107° (from aqueous alcohol).

3.742 mg substance: 0.323 ml N_2 (20.5°, 742 mm).
Found %: N 9.81.
$C_{15}H_{22}ON_2S$. Computed %: N 10.07.

SUMMARY

1. A number of C-alkyl-substituted morpholines (2-methyl-morpholine, 3-methylmorpholine, 2,5-dimethylmorpholine, 3,5-dimethylmorpholine, 2-ethylmorpholine,

2-ethyl-5-methylmorpholine, and 2,6-diethylmorpholine) have been synthesized by dehydrating the respective dialkanolamines.

2. The initial dialkanolamines were produced by condensing α-olefin oxides with ammonia or with monoalkanolamines.

LITERATURE CITED

[1] J.Payman, H.Piggot, British patent 298336; Zbl., 1929, 1, 1616.

[2] French Patent 804193 (1936); Zbl., 1937, 1, 2262.

[3] British patent 362060 (1931); Zbl., 1933, 1, 4042.

[4] K.A.Krasusky, J.Gen.Chem., 6, 460 (1936).

[5] A.N.Nesmeyanov and I.F.Lutsenko, Izv. USSR Acad. Sci., 4, 296 (1943).

[6] L.Medard, Bull. Soc. chim. (5), 3, 138 (1936).

[7] L.Knorr, Ber., 32, 729 (1899).

[8] K.A.Krasusky, J. prak. Chem., 115, 315 (1927).

[9] W.Horne, R.Shriner, J. Am. Chem. Soc., 54, 2925 (1932).

[10] A.Ya.Berlin, T.P.Sycheva, J.Gen. Chem., 20, 577 (1950).*

[11] Cottle, Ieltsch, Stoudt, Walters, J. Org. Chem., 11, 286 (1946).

[12] G.Gabriel, Ber., 49, 2121 (1916).

Received October 9, 1948.

*See CB translation p. 609 ff.

108. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS. V. COMPLETE SYNTHESIS OF A STEREOISOMER OF 15-METHYLANDROSTENEDIONE

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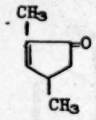
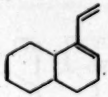
Institute of Organic Chemistry of the USSR Academy of Sciences

Diene condensations with α,β-unsaturated cyclic ketones have been investigated systematically in our laboratory recently with a view to the employment of these reactions for the synthesis of steroid compounds. It has been shown that 1,3-dimethyl--1-cyclopenten-5-one (I), synthesized in our laboratory and made available, enters fairly readily into a diene synthesis with vinylcyclohexene (II) and vinyloctalin (III), giving rise to the respective polycyclic ketones (IV) and (V), which contain the cyclopentanone ring with an angular methyl group [1]:

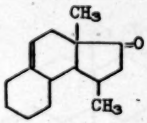


(I)

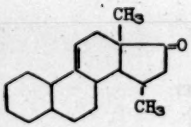
(II)



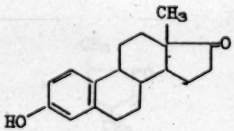
(III)



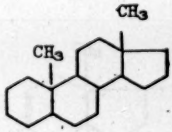
(IV)



(V)



(VI)

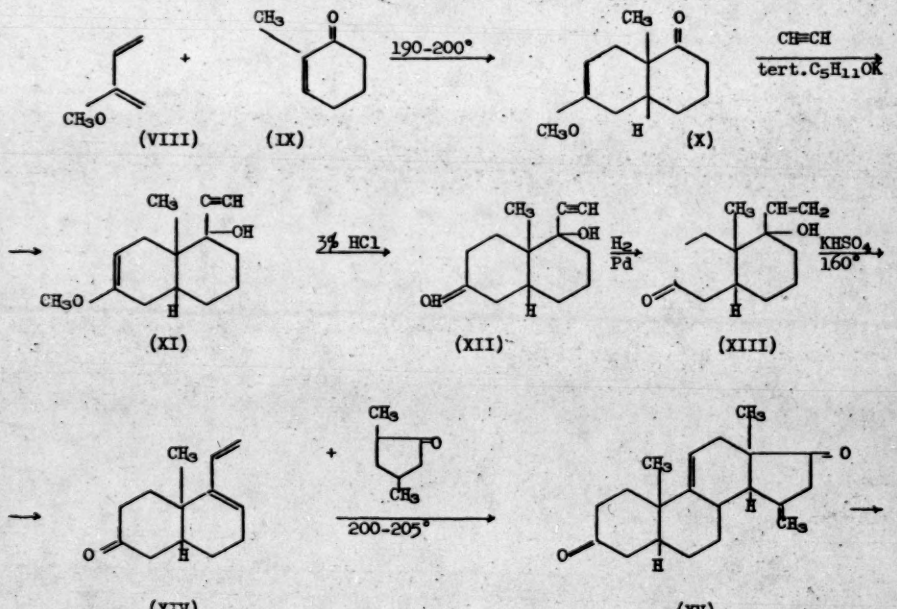


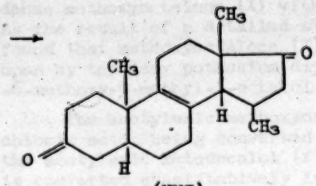
(VII)

The importance of these diene condensations lies in the fact that they open up broad and tempting possibilities of the simplest synthesis of steroid compounds, which belong to one of the most interesting groups of biologically active substances created by nature, which play an essential and manysided role in the activity of animal and plant organisms.

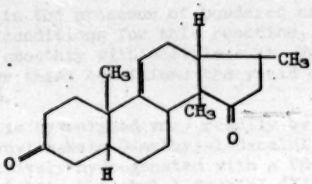
In recent years estrone (VI) and its related compounds have been succesafully synthesized [2]. But repeated attempts to synthesize compounds with the structure of androstane (VII) have met with no success [3]. Syntheses of this sort present a problem that is much more complicated than the synthesis of estronic products, inasmuch as it necessitates the introduction of a spare angular methyl group and results in the formation of compounds with a large number of asymmetrical carbon atoms. Up to the present time the synthesis of compounds of the androstane series remains one of the important unsolved and difficult problems of organic chemistry.

After prolonged research, involving the overcoming of a number of experimental difficulties, we have succeeded in developing a rather simple and convenient method for synthesizing compounds with an androstane skeleton. This method is based upon diene condensation with α,β-unsaturated cyclic ketones, to the investigation of which our laboratory has devoted considerable effort over the past five years. In the present paper we describe the complete synthesis of a stereoisomer of 15-methylandrostene-3,17-dione (XVI), achieved by us as follows:





(XVI)



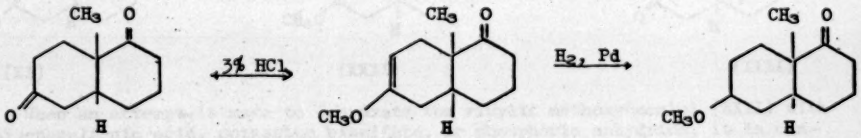
(XVII)

After a detailed study of the diene condensation of 2-methoxybutadiene (VIII) with 1-methyl-Δ^1-cyclohexen-6-one (IX), the conditions were found under which cis-Δ^9--6-methoxy-9-methyl-1-octalone (X) is formed with a yield of 25%, based on the reacted methylcyclohexenone. The chief obstacles to this reaction are dimerization and polymerization of the methoxybutadiene. That is why the reaction must be carried out in a solution of a large excess of methylcyclohexenone at a temp. of 190-210°.

At lower temperatures the diene condensation takes place so slowly, compared to the dimerization and polymerization of methoxybutadiene, that no perceptible quantity of the octalone (X) can be secured.

The structure of methoxyoctalone (X), especially the position of the methoxy group, may be considered to be proved beyond question, based upon the fact that when methoxybutadiene (VIII) is condensed with α,β-unsaturated ketones, the only compounds formed are para-substituted methoxy cyclohexenyl ketones, as has been shown in numerous examples in our laboratory [3] as well as by other authors [4]:

Methoxyoctalone (X) partially hydrolyzes even when it is exposed to the air. In the presence of dilute mineral acids it is wholly converted into crystalline cis-1,6-diketo-9-methyldecalin (XVIII). In the presence of a Pd catalyst, methoxyoctalone (X) adds one molecule of hydrogen, giving rise to 6-methoxy-9-methyl-1-decalone (XIX).



(XVIII) (X) (XIX)

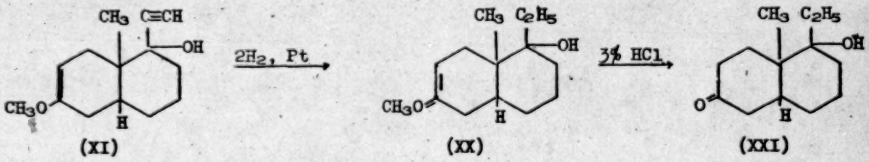
With a Pt catalyst, methoxyoctalone (X), like similar compounds that contain a methoxy group at the double bond in the ring, is not hydrogenated at all, practically speaking.

In contrast to other alicyclic and aliphatic ketones, it is difficult to con-

dense methoxyoctalone (X) with acetylene in the presence of powdered caustic potash. As the result of a detailed study of the conditions for this reaction, it has been found that methoxyoctalone (X) condenses smoothly with acetylene at -70° when acted upon by tertiary potassium amylate. Under these conditions the yield of 1-ethynyl--6-methoxy-9-methyl-1-octalol (XI) is 80%.

The acetylenic methoxyoctalol (XI) is hydrolyzed very readily by dilute hydrochloric acid, being converted into 1-ethynyl-6-keto-9-methyl-1-decalol (XII). When the acetylenic ketodecalol (XII) is selectively hydrogenated with a Pd catalyst, it is converted quantitatively into 1-vinyl-6-keto-9-methyl-1-decalol (XIII).

When the acetylenic methoxyoctalol (XI) is hydrogenated with a Pt catalyst, it adds only two molecules of hydrogen at the triple bond, giving rise to 1-ethyl--6-methoxy-9-methyloctalol (XX), hydrolysis of which yields 1-ethyl-6-keto-9-methyl--1-decalol (XXI):

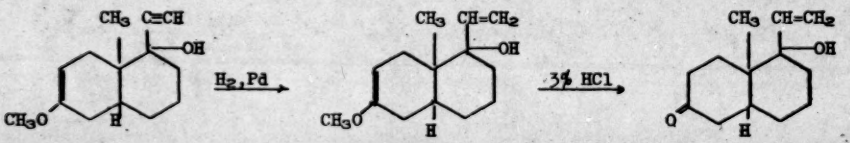


(XI) (XX) (XXI)

The ethylketodecalol (XXI) was likewise synthesized by the exhaustive hydrogenation of the acetylenic ketodecalol (XII).

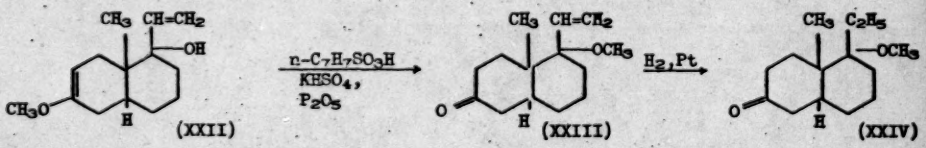
Thus, the double bond carrying the methoxy group in the acetylenic methoxyoctalol (XI) cannot be hydrogenated with an Adams Pt catalyst, exactly as was the case with the methoxyoctalol (X)

When selectively hydrogenated with a Pd catalyst (1 mol of H_2), the acetylenic methoxyoctalol (XI) yields 1-vinyl-6-methoxy-9-methyl-1-octalol (XXII), hydrolysis of which yields the vinylic ketodecalol (XIII), that is identical with the product of the selective hydrogenation of the acetylenic ketodecalol (XII).



(XI) (XXII) (XIII)

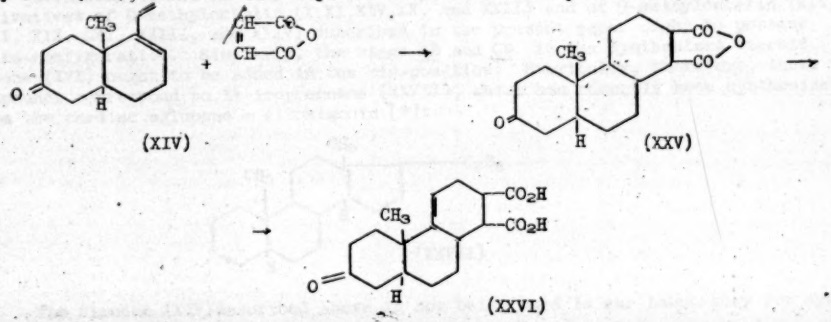
When an attempt is made to dehydrate the vinylic methoxydecalol (XXII) with p-toluenesulfonic acid, potassium bisulfate, or phosphoric anhydride, it is converted into an isomeric vinylic keto ether (XXIII), which absorbs one molecule of hydrogen during hydrogenation, forming a saturated keto ether (XXIV):



(XXII) (XXIII) (XXIV)

An analogous isomeric transformation of an unsaturated methoxy alcohol into the corresponding methyl ether of the keto alcohol will be described in the following report, using acetylene derivatives of the hydrindan series as examples. Thus, the vinylic methoxyoctalol (XXII) proved to be quite incapable of normal dehydration in the presence of acid agents. Nor did an endeavor to dehydrate the methoxyoctalol (XXII) by Chugayev's xanthogenate method meet with any success, and so we turned to an examination of the dehydration of the vinylic ketodecalol (XIII). We found that the vinylic ketodecalol (XIII) dehydrates fairly smoothly when it is heated with powdered potassium bisulfate, producing 1-vinyl-6-keto-9-methyl-$\Delta^{1,2}$-octalin (XIV) with a yield of some 70%.

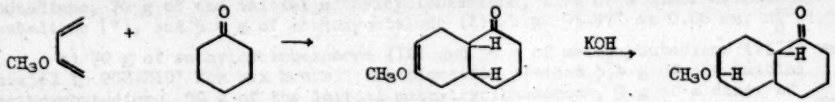
The dienone (XIV) condenses with maleic anhydride even at room temperature (with the evolution of heat), resulting in a nearly quantitative yield of the anhydride (XXV), which is then saponified to the dicarboxylic acid (XXVI):



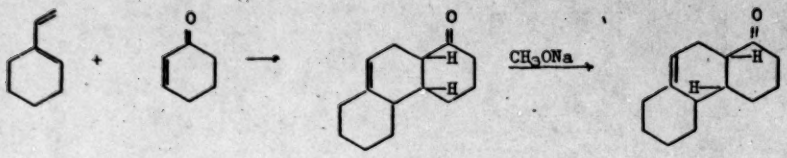
(XIV) (XXV) (XXVI)

When the dienone (XIV) was heated to 200-205° for six hours with ten times its weight of dimethylcyclopentenone (I), we secured a yield of 40% of the stereoisomer $\Delta^{8,9}$-15-methylandrostenedione (XVI), which was formed by the thermal isomerization of the normal product of the diene synthesis, i.e., $\Delta^{9,11}$-15-methylandrosten-3,17-dione (XV), together with a shift of the double bond. The position of the double bond in methylandrostenedione (XVI) is based upon the circumstance that this ketone is wholly incapable of being hydrogenated with a Pt catalyst in a solution of glacial acetic acid, even at high temperature (100°), whereas polycyclic ketones of the (XV) type, which possess a semicyclic double bond, are readily hydrogenated under these conditions. Nor is it impossible that when the dienone (XIV) is condensed with dimethylcyclopentenone, a structural isomer of methylandrostenedione (XVII) may also be formed; we shall endeavor to resolve this question in subsequent reports.

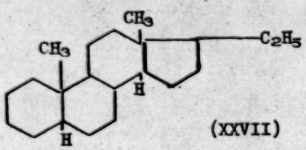
In the research on the condensation of dienes with Δ^2-cyclohexenone conducted in our laboratory, it was shown* that only cis-isomers are formed, which are quantitatively isomerized to the trans-forms by the action of alkaline agents:



*Cf the next report in this issue of the Journal.



According to the principle of cis-addition during diene synthesis, all the derivatives of 9-methyloctalin (X,XI,XIV,XX, and XXII) and of 9-methyldecalin (XII, XIII, XIX, XXI, XXIII, and XXIV) described in the present paper ought to possess a cis-configuration. Similarly, the rings AB and CD in the synthesized steroid ketone (XVI) ought to be added in the cis-position. Sterically, therefore, these compounds correspond to 14-isopregnane (XXVII), which has recently been synthesized from the cardiac aglucone - gitoxigenin [9]:



(XXVII)

The dienone (XIV) described above is now being used in our laboratory for systematic syntheses of steroid compounds.

EXPERIMENTAL

2-Methoxy-1,3-butadiene (b.p. 74.8-75.3°; n_D^{20} 1.4438) was prepared by adding methanol to vinylacetylene, after which the methanol was detached from the 1,3,3-trimethoxybutane by potassium bisulfate [6,7]. 1-Methyl-Δ^1-cyclohexen-6-one (b.p. 65-67° at 16 mm; n_D^{20} 1.4812) was synthesized from o-methylcyclohexanone by a method elaborated by us, which will be described in one of our next reports. 1,3-Dimethyl-Δ^1-cyclopenten-5-one (b.p. 53-54° at 10 mm; n_D^{20} 1.4660) was synthesized by hydrating vinylisopropenylacetylene and cyclizing the resulting allyl isopropenyl ketone with phosphoric acid [8].

Diene condensation of 2-methoxy-1,3-butadiene with 1-methyl-Δ^1-cyclohexen-6-one. These tests were run in an atmosphere of carbon dioxide within a metallic autoclave, in the presence of 0.5% of pyrogallol.

a) 80 g of methylcyclohexenone (IX) and 40 g of methoxybutadiene (VIII) were heated to 215° for three hours. Fractionation yielded 13 g of the initial methoxybutadiene, 70 g of the initial methylcyclohexenone, 11 g of a dimer of methoxybutadiene [7], and 5.4 g of methoxyoctalone (X); b.p. 95-97° at 0.06 mm; n_D^{20} 1.5103.

b) 70 g of methylcyclohexenone (IX) and 35 g of methoxybutadiene (VIII) were heated to 208-210° for six hours. Fractionation yielded 3.4 g of the initial methoxybutadiene, 59 g of the initial methylcyclohexenone, 9 g of a dimer of methoxybutadiene, and 4.6 g of methoxyoctalone (X); b.p. 115-117° at 0.2 mm; n_D^{20} 1.5116

c) 20 g of methylcyclohexenone (IX) and 7 g of 2-methoxybutadiene were heated to 190° for 40 hours. This yielded 14.5 g of the initial methylcyclohexenone, 5.6 g of a dimer of methoxybutadiene, and 2 g of methoxyoctalone (X); b.p. 98-102° at 0.1 mm; n_D^{20} 1.5078.

Analysis of Δ^6-9-methyl-6-methoxy-1-octalone (X). The diene condensation products recovered in the above series of experiments, were combined and refractionated. This yielded 19 g of Δ^6-9-methyl-6-methoxy-1-octalone (X) as a viscous, pale yellow liquid with a slight odor of camphor; b.p. 102° at 0.14 mm; n_D^{20} 1.5092.

4.315 mg substance: 11.752 mg CO_2; 3.597 mg H_2O.
4.280 mg substance: 11.667 mg CO_2; 3.540 mg H_2O.
Found %: C 74.3, 74.4; H 9.3, 9.2.
$C_{12}H_{18}O_2$. Computed %: C 74.2; H 9.3.

The semicarbazone of the methoxyoctalone (X), prepared in absolute methanol and recrystallized from absolute ethyl alcohol, fused at 204°.

4.270 mg substance: 0.620 ml N_2 (22°, 755 mm).
3.690 mg substance: 0.543 ml N_2 (22°, 755 mm).
Found %: N 16.7, 16.8.
$C_{13}H_{21}O_2N_3$. Computed %: N 16.7.

Hydrogenation of Δ^6-9-methyl-6-methoxy-1-octalone. 1.4 g of the methoxyoctalone (X) was hydrogenated over a Pd catalyst in a solution of absolute ether. During 10 hours 140 ml of hydrogen was absorbed (155 ml was called for). Fractionation yielded 1.1 g of 9-methyl-6-methoxy-1-decalone (XIX) as a viscous, colorless liquid; b.p. 125-128° at 5 mm; n_D^{20} 1.5030.

The semicarbazone of the synthesized methoxydecalone (XIX) fused at 209.5° (in a sealed capillary) after recrystallization from alcohol.

3.640 mg substance: 0.529 ml N_2 (19°, 734 mm).
4.290 mg substance: 0.631 ml N_2 (20°, 737 mm).
Found %: N 16.5, 16.6.
$C_{13}H_{23}O_2N_3$. Computed %: N 16.6.

Hydrolysis of Δ^6-9-methyl-6-methoxy-1-octalone. 2 g of the methoxyoctalone (X) was shaken up for three hours with 10 ml of 3% hydrochloric acid. The mixture was saturated with ammonium chloride and extracted with ether, and the ether solution was neutralized with a 5% soda solution and desiccated with sodium sulfate. Fractionation yielded a substance with a b.p. of 152° at 3 mm, which crystallized in the receiver. Recrystallization from benzene yielded 1.3 g of 9-methyl-1,6-diketodecalin (XVIII) as colorless platelets with a m.p. of 57°.

5.355 mg substance: 14.392 mg CO_2; 4.217 mg H_2O.
5.420 mg substance: 14.547 mg CO_2; 4.310 mg H_2O.
Found %: C 73.3, 73.2. H 8.8, 8.9.
$C_{11}H_{16}O_2$. Computed %: C 73.3; H 8.9.

The disemicarbazone of the synthesized diketodecalin (XVIII), which was insoluble in organic solvents, fused at 221-222° with decomposition (in a sealed capillary) after repeated washings with water, ether, and alcohol.

1.296 mg substance: 0.326 ml N_2 (22°, 752 mm).
1.097 mg substance: 0.277 ml N_2 (22°, 752 mm).
Found %: N 28.7, 28.9.
$C_{13}H_{22}O_2N_8$. Computed %: N 28.6.

Condensation of Δ^8-9-methyl-6-methoxy-1-octalone with acetylene. A solution of 19 g of the methoxyoctalone (X) in 50 ml of absolute ether was saturated at -70° with anhydrous acetylene for 45 minutes. With constant stirring, while more acetylene was passed through the solution, a mixture of 20 g of metallic potassium dissolved in 100 ml of anhydrous tertiary amyl alcohol and 50 ml of ether was added. The stirring and passage of acetylene through the mixture was continued for six hours at -70° and for two hours the next day at room temperature. 30 ml of water was added to the mixture, the ether solution was removed, the aqueous layer was extracted with ether, and the combined ether solutions were neutralized by passing carbon dioxide through the solution and then desiccated with magnesium sulfate. Vacuum distillation in a current of anhydrous nitrogen yielded 17.4 g of 1-ethynyl-6-methoxy-9-methyl-1-octalol (XI) as a viscous, colorless liquid, which dissolves with difficulty in ether and yields a copious precipitate with ammoniacal silver nitrate; b.p. 114-116° at 0.07 mm; n_D^{20} 1.5248. Before analysis the substance was dessicated for 40 hours in vacuum over phosphoric anhydride.

4.195 mg substance: 11.700 mg CO_2; 3.460 mg H_2O.
4.095 mg substance: 11.400 mg CO_2; 3.380 mg H_2O.
Found %: C 76.2, 76.1; H 9.2, 9.2.
$C_{14}H_{20}O_2$. Computed %: C 76.3; H 9.1.

Hydrogenation of 1-ethynyl-6-methoxy-9-methyl-1-octalol. During hydrogenation over a Pt catalyst, 0.6 g of the acetylenic alcohol (XI) absorbed 123 ml of hydrogen (2 mols). Fractionation in an atmosphere of anhydrous nitrogen yielded 1-ethyl-6-methoxy-9-methyl-1-octalol (XX) as a viscous, colorless liquid; b.p. 104-108° at 0.1 mm; n_D^{20} 1.5146.

5.040 mg substance: 13.757 mg CO_2; 4.920 mg H_2O.
7.950 mg substance: 21.727 mg CO_2; 7.540 mg H_2O.
Found %: C 74.5, 74.6; H 10.9, 10.6.
$C_{14}H_{24}O_2$. Computed %: C 75.0; H 10.7.

Hydrolysis of 1-ethyl-6-methoxy-9-methyl-1-octalol. 0.5 g of the methoxyoctalol (XX) was agitated for an hour with 5 ml of 3% hydrochloric acid. The mixture was saturated with ammonium chloride, and the product was extracted with ether, neutralized with a 5% soda solution and desiccated with magnesium sulfate. Driving off the ether yielded 0.3 g of 1-ethyl-6-keto-9-methyl-1-decalol (XXI), which crystallized when kept over phosphoric anhydride in vacuum. The crystals fused at 102° after recrystallization from petroleum ether.

4.440 mg substance: 12.112 mg CO_2; 4.290 mg H_2O.
4.670 mg substance: 12.710 mg CO_2; 4.480 mg H_2O.
Found %: C 74.4, 74.3; H 10.8, 10.7.
$C_{13}H_{22}O_2$. Computed %: C 74.4; H 10.5.

The semicarbazone of the keto alcohol (XXI) fused with decomposition at 226-228° after recrystallization from alcohol.

4.270 mg substance: 0.620 ml N_2 (22°, 755 mm).
3.690 mg substance: 0.543 ml N_2 (22°, 755 mm).
Found %: N 16.6, 16.8.
$C_{14}H_{25}O_2N_3$. Computed %: N 15.7.

Hydrolysis of 1-ethynyl-6-methoxy-9-methyl-1-octalol. 12 g of the acetylenic alcohol (XI) was agitated for one hour with 15 ml of 5% hydrochloric acid. The resulting colorless crystals (8 g) were filtered out and recrystallized from a mixture of petroleum ether and alcohol. The crystals of 1-ethynyl-6-keto-9-methyl-1-decalol

(XII) fused at 158° after being desiccated in vacuum over phosphoric anhydride. The keto alcohol (XII) dissolves with difficulty in ether, somewhat better in dioxane, and readily in alcohol.

5.880 mg substance: 16.320 mg CO_2; 4.290 mg H_2O.
5.630 mg substance: 15.565 mg CO_2; 4.480 mg H_2O.
Found %: C 75.7, 75.5; H 8.8, 8.8.
$C_{13}H_{18}O_2$. Computed %: C 75.7; H 8.7.

The semicarbazone of the synthesized keto alcohol (XII) fused with decomposition at 232° after recrystallization from alcohol.

3.650 mg substance: 0.522 ml N_2 (24°, 745 mm).
4.200 mg substance: 0.588 ml N_2 (23°, 752 mm).
Found %: N 16.11, 15.98.
$C_{14}H_{11}O_2N_3$. Computed %: N 15.94.

The mother liquor remaining after hydrolysis of the acetylenic carbinol (XI) was saturated with ammonium chloride and extracted with ether; the ether solution was washed with a 5% soda solution and desiccated with magnesium sulfate. After the ether had been driven off, we secured 2 g of a substance with a b.p. of 134-137° at 0.5 mm as a viscous, pale-yellow paste, which did not crystallize when kept in vacuum over phosphoric anhydride. This fraction, which yields a voluminous precipitate with ammoniacal silver nitrate, is apparently a somewhat contaminated isomer of the acetylenic keto alcohol (XII).

6.370 mg substance: 17.411 mg CO_2; 5.200 mg H_2O.
6.930 mg substance: 18.937 mg CO_2; 5.800 mg H_2O.
Found %: C 74.6, 74.6; H 9.1, 9.3.
$C_{13}H_{18}O_2$. Computed %: C 75.7; H 8.7.

Exhaustive hydrogenation of 1-ethyl-6-keto-9-methyl-1-decalol. 0.5 g of the acetylenic keto alcohol (XII) absorbed 105 ml of hydrogen (2 mols) when hydrogenated over a Pt catalyst in a solution of ethyl alcohol. Driving off the alcohol left a viscous, colorless residue, which crystallized slowly when kept in vacuum over phosphoric anhydride. The crystals fused at 101-102° after recrystallization from petroleum ether. A test sample mixed with a sample of 1-ethyl-6-keto-9-methyl-1-decalol (XXI) produced by hydrolyzing the methoxyoctalol (XX) exhibited no depression of the melting point.

Synthesis of 1-vinyl-6-methoxy-9-methyl-1-octalol. 15.64 g of the acetylenic alcohol (XI) was hydrogenated in 25 ml of absolute ether over a Pd catalyst until 1560 ml of hydrogen (1 mol) had been absorbed. Fractionation yielded 15.1 g of 1-vinyl-6-methoxy-9-methyl-1-octalol (XXII) as a viscous, colorless liquid, which yields no precipitate with ammoniacal silver nitrate: b.p. 113-115° at 0.02 mm; n_D^{20} 1.5198.

4.360 mg substance: 12.080 mg CO_2; 3.930 mg H_2O.
Found %: C 75.6; H 10.10.
$C_{14}H_{22}O_2$. Computed %: C 75.7; H 9.9.

Synthesis of 1-vinyl-6,9-methyl-1-decalol (XIII). a) Hydrolysis of 1-vinyl-6-methoxy-9-methyl-1-octalol (XXII). Hydrolyzing 4 g of the vinylic methoxyoctalol (XXII) with 3% hydrochloric acid yielded 3.1 g of 1-vinyl-6-keto-9-methyl-1-decalol (XIII); b.p. 131-135° at 0.3 mm; n_D^{20} 1.5141.

4.360 mg substance: 11.940 mg CO_2; 3.840 mg H_2O.
7.130 mg substance: 19.467 mg CO_2; 6.232 mg H_2O.
Found %: C 74.7, 74.5; H 9.8, 9.8.
$C_{13}H_{20}O_2$. Computed %: C 75.0; H 9.6.

The 2,4-Dinitrophenylhydrazone of the synthesized keto alcohol fused at 131° after recrystallization from a mixture of ethyl acetate and alcohol.

3.635 mg substance: 0.460 ml N_2 (23°, 759 mm).
4.277 mg substance: 0.543 ml N_2 (23°, 739 mm).
Found %: N 14.6, 14.2.
$C_{19}H_{24}O_5N_4$. Computed %: N 14.4.

b) Selective hydrogenation of 1-ethynyl-6-keto-9-methyl-1-decalol (XII). 7.23 g of the acetylenic ketodecalol (XII) was hydrogenated over a Pd catalyst in ethyl alcohol. 780 ml of hydrogen (1 mol = 786 ml) was absorbed during 55 minutes. Fractionation yielded 6.5 g of a substance with a b.p. of 120-135° at 0.5 mm; n_D^{20} 1.5030. (n_D^{20} of the last drop was 1.5162.) This substance was 1-vinyl-6-keto-9-methyl-1--decalol (XIII), which apparently retains some ethyl alcohol. The substance yields a 2,4-dinitrophenylhydrazone, which fuses at 130-132° after recrystallization from an alcohol – ethyl acetate mixture and exhibits no depression when mixed with a test sample of the substance synthesized in Experiment (a).

Isomerization of 1-vinyl-6-methoxy-9-methyl-1-octalol. a) 0.8 g of phosphoric anhydride was added in three batches, with stirring, to 2.2 g of the vinylic methoxyoctalol (XXII) dissolved in 5 ml of anhydrous acetone. Stirring was continued for twenty minutes in the cold and twenty minutes at 50°. The mixture was diluted with 10 ml of water, extracted with ether, and desiccated with magnesium sulfate. Fractionation yielded 1.4 g of 1-methoxy-1-vinyl-6-keto-9-methyldecalin (XXIII) as a colorless, mobile liquid with a b.p. of 101-103° at 0.1 mm; n_D^{20} 1.5042.

b) 1.4 g of the vinylic methoxyoctalol (XXII) and 0.05 g of p-toluenesulfonic acid were heated to 110-115° for 40 minutes. The reaction mixture was diluted with 5 ml of water and extracted with ether; the ether layer was removed and desiccated with magnesium sulfate. Fractionation yielded 0.6 g of the keto ether (XXIII) with a b.p. of 106-110° at 0.1 mm; n_D^{20} 1.5040.

c) 1.8 g of vinylic methoxyoctalol (XXII) and 0.9 g of anhydrous powdered potassium bisulfate were heated to 120° in a 100-mm vacuum for 30 minutes. Vacuum fractionation yielded 1.1 g of the keto ether (XXIII) with a b.p. of 94-97° at 0.02 mm; n_D^{20} 1.5010.

5.750 mg substance: 15.965 mg CO_2; 5.125 mg H_2O.
Found %: C 75.8; H 9.9.
$C_{14}H_{22}O_2$. Computed %: C 75.7; H 9.9.
Found according to Zeisel %: OCH_3 14.11, 14.19.
$C_{14}H_{22}O_2$. Computed %: OCH_3 13.95.

Subjecting the substance to the Chugayev-Tserevitinov test indicated that no hydroxyl groups were present. Compound (XXIII) does not reduce ammoniacal silver nitrate and produces no color when treated with Schiff's reagent.

The 2,4-dinitrophenylhydrazone of the synthesized keto ether (XXIII) fused at 137-138° after recrystallization from an alcohol-benzene mixture.

3.270 mg substance: 0.382 ml N_2 (23°, 768 mm).
4.230 mg substance: 0.507 ml N_2 (22°, 757 mm).
Found %: N 13.6, 13.8.
$C_{20}H_{26}O_5N_4$. Computed %: N 13.9.

Hydrogenation of 1-methoxy-1-vinyl-6-keto-9-methyldecalin. During hydrogenation with a Pt catalyst in ethyl alcohol, 0.47 g of the keto ether (XXIII) absorbed 58 ml (1 mol) of hydrogen. Distillation yielded 0.3 g of a colorless liquid; b.p. 97-100° at 0.15 mm; n_D^{20} 1.4943.

6.920 mg substance: 18.920 mg CO_2; 6.610 mg H_2O.
5.610 mg substance: 15.337 mg CO_2; 5.412 mg H_2O.
Found %: C 74.6, 74.6; H 10.7, 10.8.
$C_{14}H_{24}O_2$. Computed %: C 75.0; H 10.7.

Attempt to dehydrate the vinylic methoxyoctalol (XXII) by Chugayev's xanthogenate method. 0.5 g of metallic potassium was added in small batches to a solution of 2.5 g of the alcohol (XXII) in 10 ml of absolute xylene, and the evolution of hydrogen was observed to be moderate. The mixture was heated to 125° for two hours in a small flask fitted with a reflux condenser and closed with a tube containing calcium chloride. 1.6 g of anhydrous hydrogen sulfide was added drop by drop to the mixture, decanted to eliminate the unreacted potassium and diluted with 10 ml of ether; this was accompanied by the evolution of considerable heat. The pasty mass was heated for one hour until the ether boils gently, after which 2.5 g of methyl iodide was added, and heating was continued for two more hours. The precipitate of potassium iodide was filtered out of the mixture, which was distilled at 2 mm and a bath temperature of 150-170°, after the solvent had been driven off. This yielded 0.8 g of a substance with a b.p. of 124-128° at 2 mm; n_D^{20} 1.5260. The synthesized product does not react with maleic anhydride when heated to 150° for two hours.

Dehydration of 1-vinyl-6-keto-9-methyldecalol (XIII). 1.7 g of the vinylic ketodecalol (XIII) and 0.9 g of anhydrous powdered potassium bisulfate were placed in a small Claisen flask and heated in a 60-mm vacuum over a metal bath. Water began to be evolved at 160°. Heating was continued at this temperature for 30 minutes, the water was driven off at 1 mm, and the mixture was distilled with a preliminary vacuum. This yielded 0.8 g of 1-vinyl-6-keto-9-methyl-$\Delta^{1,2}$-octalin (XIV) as a colorless mobile liquid; b.p. 100-102° at 0.1 mm; n_D^{20} 1.5302.

The semicarbazone of the synthesized dienone (XIV) fused with decomposition at 226-227° after recrystallization from alcohol.

3.795 mg substance: 0.560 ml N_2 (23°, 759 mm).
3.490 mg substance: 0.516 ml N_2 (23°, 754 mm).
Found %: N 17.0, 16.9.
$C_{14}H_{21}ON_3$. Computed %: N 17.0.

Condensation of the dienone (XIV) with maleic anhydride. 1.5 g of the dienone (XIV) and 0.8 g of maleic anhydride were placed in a glass ampoule. Mixture of the components was accompanied by the evolution of heat, the mixture turned yellow, and part of the maleic anhydride dissolved. The mixture was heated to 120° for 2 hours in the sealed ampoule. The unreacted excess maleic anhydride was driven off at 0.1 mm. The remaining viscous semicrystalline mass was agitated at 80° for 20 minutes with 10 ml of 5% hydrochloric acid. The crystals that settled out dissolved during neutralization with sodium bicarbonate. The slight organic layer that floated on top after neutralization was removed, and the aqueous layer was extracted with ether. When the aqueous layer was acidulated, white crystals settled out as lustrous platelets. Recrystallization from petroleum ether yielded 1.4 g of 7-keto-13-methyldodecahydrophenanthrene-1,2-dicarboxylic acid (XXVI); b.p. 202°:

4.290 mg substance: 10.477 mg CO_2; 2.695 mg H_2O.
1.550 mg substance: 3.785 mg CO_2; 1.005 mg H_2O.
Found %: C 66.64, 66.64; H 7.0, 7.2.
$C_{17}H_{22}O_4$. Computed %: C 66.7; H 7.2.
0.1512 g substance: 10.0 ml 0.1 N KOH
Found: M 301.
$C_{17}H_{22}O_4$. Computed: M 306.

The semicarbazone of the synthesized keto acid fused with decomposition at 238-239° (in a sealed capillary) after recrystallization from alcohol.

4.810 mg substance: 0.497 ml N_2 (23°, 750 mm).
4.795 mg substance: 0.500 ml N_2 (23°, 751 mm).
Found %: N 11.76, 11.88.
$C_{18}H_{25}O_5N_3$. Computed %: N 11.88.

Condensation of the dienone (XIV) with 1,3-dimethyl-1-cyclopenten-5-one. 2.2 g of the dienone (XIV) and 22 g of the dimethylcyclopentenone (I) were heated with pyrogallol in a metallic ampoule to 200-205° for 6 hours. The unchanged excess of the cyclopentenone (20 g) was driven off in vacuum, after which crystals settled out of the residue. This yielded 1.2 g of crystals of the stereoisomer of $\Delta^{8,9}$-15-methylandrostenedione (XVI) as white platelets, which fused at 163° after recrystallization from a mixture of petroleum ether and benzene.

4.095 mg substance: 12.020 mg CO_2; 3.405 mg H_2O.
2.990 mg substance: 8.745 mg CO_2; 2.480 mg H_2O.
Found %: C 80.1, 79.8; H 9.3, 9.3.
$C_{20}H_{28}O_2$. Computed %: C 80.0; H 9.3.

The monosemicarbazone of the synthesized diketone dissolves with difficulty in organic solvents. The semicarbazone was purified by washing it with hot water, alcohol, and ether, after which it fused at 219-221°.

4.009 mg substance: 0.423 ml N_2 (23°, 739 mm).
5.055 mg substance: 0.512 ml N_2 (23°, 741 mm).
Found %: N 11.6, 11.4.
$C_{21}H_{31}O_2N_3$. Computed %: N 11.7.

0.25 g of the diketone (XVI) in 8 ml of absolute dioxane did not absorb hydrogen when shaken with an Adams Pt catalyst at room temperature or at 100°. Nor was hydrogen absorbed when an endeavor was made to hydrogenate the diketone (XVI) in glacial acetic acid with a Pt catalyst, either at room temperature or at 100°.

SUMMARY

The stereoisomer of $\Delta^{8,9}$-15-methylandrosten-3,17-dione has been completely synthesized, and a general procedure has been elaborated for the synthesis of androstane steroids.

LITERATURE CITED

[1] I.N.Nazarov and T.D.Nagibina, J.Gen.Chem., 18, 1090 (1948); I.N.Nazarov and T.D.Nagibina, J.Gen.Chem. 20, No. 3 (1950)*.

[2] Anner, Miescher Experientia, IV, 25 (1948); Bachmann, Cole, Wilds, J.Am. Chem. Soc., 62, 2084 (1940); Bachmann, Kushner, Stevenson, J.Am.Chem. Soc., 64, 974 (1942); Johnson, Peterson, Gutsche, J.Am.Chem.Soc., 69, 2942 (1947); Wilds, Johnson, J.Am.Chem.Soc., 70, 1166 (1948), Robinson, Rydon, J.Chem.Soc., 1939, 1399; Dane, Schmitt, Lieb. Ann., 537, 248 (1939); Goldberg, Muller, Helv. Chim.Acta, 23, 831 (1940); Breitner, Med. u.Chem., 4, 317 (1942).

[3] Martin, Robinson, J.Chem.Soc., 1943, 491; Butz, Gaddis, J.Am.Chem.Soc., 69, 1165, 1203 (1947).

[4] A.A.Petrov, J.Gen.Chem. 11, 681 (1941); 17, 1543 (1947); Fiesselmann, Ber., 75 B, 881 (1942).

[5] I.N.Nazarov, M.V.Kuvarzina, Izv. USSR Acad.Sci., Div.Chem.Sci., 599 (1948).

[6] Dykstra, J.Am.Chem.Soc., 57, 2255 (1935).

[7] I.N.Nazarov, G.P.Verkhletova, L.D.Bergelson, Izv.USSR Acad.Sci., Div. Chem. Sci., 511 (1948).

[8] I.N.Nazarov, I.I.Zaretskaya, Izv.USSR Acad.Sci.,Div.Chem.Sci., 1, 65 (1944).

[9] Meyer, Helv. Chim. Acta, 30, 2024 (1947).

* See CB translation p. 561 ff

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DERIVATIVES OF ACETYLENE

109. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS.

VI. COMPLETE SYNTHESIS OF AN ISOMER OF 15-METHYLANDROSTEN-3,17-DIONE WITH A METHYLCYCLOPENTANE B RING

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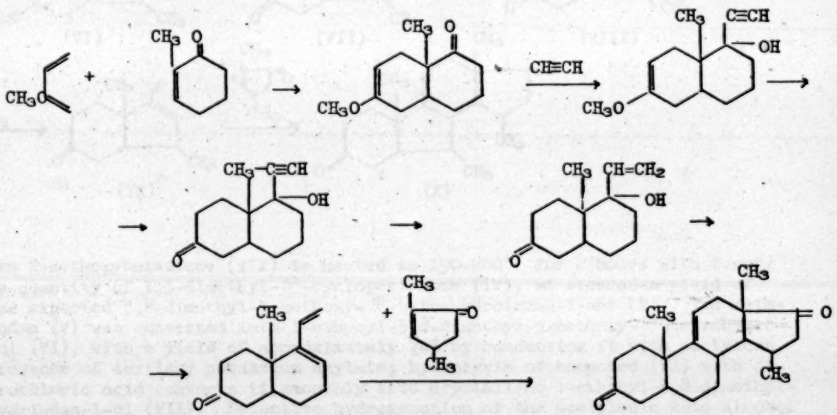
Institute of Organic Chemistry of the USSR Academy of Sciences

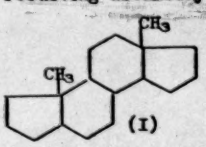
Our preceding report [1] described the complete synthesis of a stereoisomer of 15-methylandrosten-3,17-dione, effected by diene condensations with 1-methyl-Δ^4-cyclohexenone and 1,3-dimethyl-Δ^1-cyclopentenone as follows:



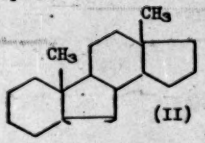
We have now made use of this simple and convenient method of synthesis to construct an isomeric androstane skeleton with a methylcyclopentane B ring.

Compounds of the A-norandrostane (I) series with a five-membered A ring and compounds of the B-norandrostane (II) series with a five-membered B ring have been often synthesized from the natural steroids by oxidizing the A and B rings and then

cyclizing the resulting dicarboxylic acids [2]:

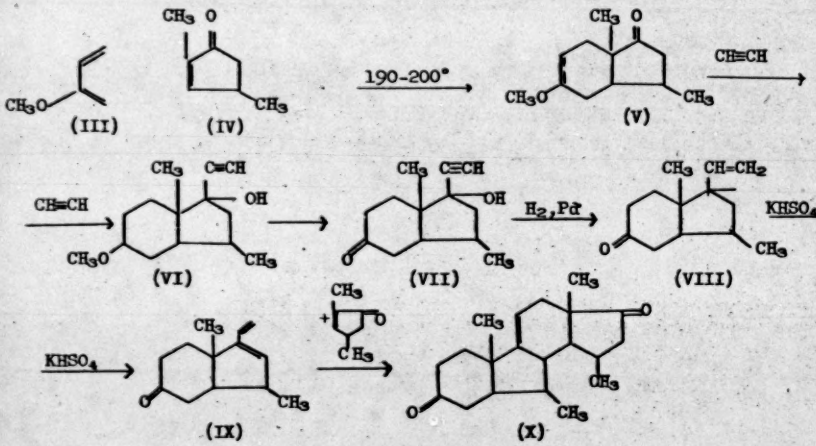


(I)

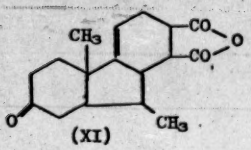


(II)

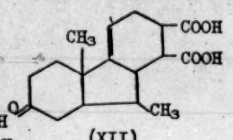
As shown in the present paper, the skeleton of B-norandrostane (II) can be built up by diene condensations with 1,3-dimethyl-Δ^1-cyclopentenone (IV), which has become an easy matter as the result of the research done in our laboratory. We effected the synthesis referred to as follows:



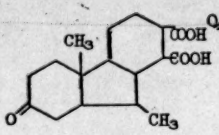
When 2-methoxybutadiene (III) is heated to 190-200° for 2 hours with twenty times its quantity of 1,3-dimethyl-Δ^1-cyclopentenone (IV), we secured a yield of 25% of the expected 3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1-one (V). The methoxyhydrindan (V) was converted into 1-ethynyl-3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1-ol (VI), with a yield of approximately 70% by condensing it with acetylene in the presence of tertiary potassium amylate; hydrolysis of compound (VI) with dilute hydrochloric acid converts it smoothly into crystalline 1-ethynyl-3,8-dimethyl-5-ketohydrindan-1-ol (VII). Selective hydrogenation of the acetylenic keto alcohol (VII) with a Pd catalyst (1 mol of H_2) converts it wholly to 1-vinyl-3,8-dimethyl-5-keto-hydrindan-1-ol (VIII), dehydration of which by means of potassium bisulfate yields about 80% of 1-vinyl-3,8-dimethyl-5-keto-Δ^1-hydrindene (IX). This diene condenses extremely readily with maleic anhydride, resulting in a nearly quantitative yield of a tricyclic fluorene keto anhydride (XI), which is converted into the respective half esters (XII or XIII) when heated with ethyl alcohol, and yields the corresponding 9,11-dimethyl-7-ketodecahydrofluorene-1,2-dicarboxylic acid (XIV) when hydrolyzed:



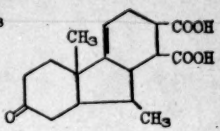
(XI)



(XII)



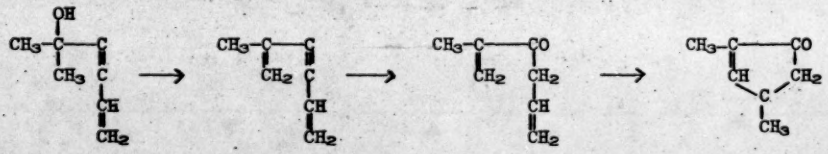
(XIII)



(XIV)

When the diene (IX) is heated to 150-160° with twenty times its weight of 1,3-dimethyl-Δ^1-cyclopentenone (IV), the expected condensation proceeds fairly smoothly, resulting in a yield of some 60% of a tetracyclic steroid diketone (X), which possesses the structure of β-norandrostane with a methylcyclopentane B ring.

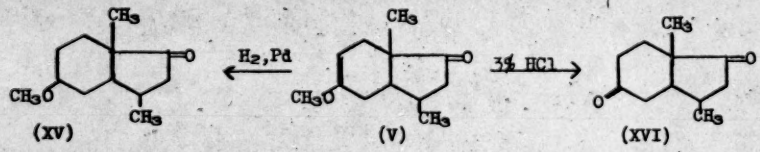
As may be seen from the foregoing equation, the whole skeleton of the steroid diketone (X) is built up entirely of acetylene, inasmuch as the methoxybutadiene (III) is produced by adding methanol to vinylacetylene, and the dimethylcyclopentenone (IV) is likewise synthesized from vinylacetylene by the method elaborated in our laboratory - via dimethylvinylethynylcarbinol and vinylisopropenylacetylene and the cyclization of the allyl isopropenyl ketone [3]:



In view of the practically unlimited availability of 1,3-dimethyl-Δ^1-cyclopentenone (IV), the synthesis of the steroid diketone (X) presents no serious difficulty.

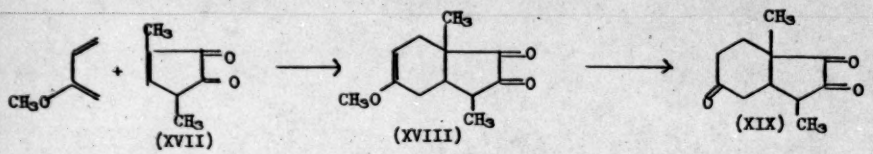
When the unsaturated methoxyhydrindone (V) is hydrogenated with a Pd catalyst, it absorbs one molecule of hydrogen and is converted into 3,8-dimethyl-5-methoxy-hydrindan-1-one (XV), which in turn may be an important intermediate product in the synthesis of steroid compounds. As in many previously discussed instances, the double bond with the methoxy group in the methoxyhydrindone (V) is not hydrogenated at all by a Pt catalyst [4,5].

When the methoxyhydrindone (V) is hydrolyzed with dilute acids, 3,8-dimethyl-hydrindan-1,5-dione (XVI), which is a simplified model of steroid compounds without B and C rings, is smoothly synthesized.



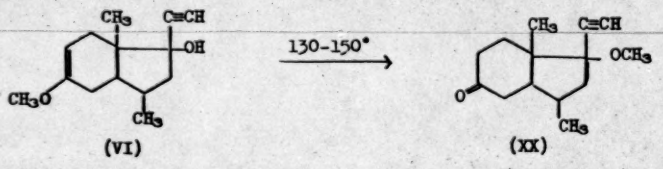
(XV) (V) (XVI)

When 2-methoxybutadiene was condensed with 1,3-dimethyl-Δ^1-cyclopenten-4,5-dione (XVII), 3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1,2-dione (XVIII), was formed, hydrolysis of which yielded the crystalline 3,8-dimethyl-hydrindan-1,2,5-trione (XIX).



(XVII) (XVIII) (XIX)

In contrast to the analogous alcohol of the octalin series, the acetylenic methoxyhydrindol (VI) is an unstable compound, gradually isomerizing even during vacuum distillation to the methyl ester of the acetylenic ketohydrindol or 3,8-dimethyl--1-ethynyl-1-methoxy-5-ketohydrindan (XX):



(VI) (XX)

Similar isomerization has likewise been described in our previous report, using as our example 1-vinyl-6-methoxy-Δ^6-1-octalol [1]:

EXPERIMENTAL

1,3-Dimethyl-Δ^1-cyclopentenone (IV) (b.p. 53-54° at 10 mm; n_D^{20} 1.4660) was synthesized by the method developed in our laboratory, involving the hydration of vinylisopropenylacetylene and the cyclization of allyl isopropenyl ketone [3]. 2-Methoxy-1,3-butadiene (b.p. 75-75.5°; n_D^{20} 1.4440) was prepared by adding methanol to vinylacetylene, after which the methanol was split off from the 1,3,3-trimethoxybutane by potassium bisulfate [4,6].

Condensation of 2-methoxy-1,3-butadiene with 1,3-dimethyl-Δ^1-cyclopentenone. 600 g of 1,3-dimethyl-Δ^1-cyclopentenone (IV), 37 g of 2-methoxy-1,3-butadiene (III), and 2 g of pyrogallol were heated to 200° in a stainless-steel autoclave for 2 hours. Fractionation yielded 586 g of unreacted 1,3-dimethyl-Δ^1-cyclopentenone (b.p. 75-77° at 32 mm; n_D^{20} 1.4670) and 18 g of 3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1-one(V):

B.p. 110-112° at 2 mm; n_D^{20} 1.4950; d_4^{20} 1.036; MR_D 54.39.
$C_{12}H_{18}O_2$. Computed: MR_D 54.50.

5.515 mg substance: 14.977 mg CO_2; 4.492 mg H_2O.
4.970 mg substance: 13.530 mg CO_2; 4.020 mg H_2O.
Found %: C 74.1, 74.3; H 9.1, 9.1.
$C_{12}H_{18}O_2$. Computed %: C 74.2; H 9.3.

The methoxyindanone (V) is a thick, colorless liquid with a slight, pleasant odor, which does not form crystalline derivatives with semicarbazide and 2,4-dinitrophenylhydrazine.

Hydrogenation of 3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1-one. 5 g of the methoxyindanone (V) in 10 ml of absolute dioxane was hydrogenated with a Pd catalyst at 100°. 570 ml of hydrogen (1 mol) was absorbed during 14 hours. Fractionation of the product yielded 4.8 g of 5-methoxy-3,8-dimethylhydrindan-1-one (XV) as a rather mobile, colorless liquid with a pleasant odor:

B.p. 110-112° at 3.5 mm; n_D^{20} 1.4782; d_4^{20} 1.012; MR_D 54.94.
$C_{12}H_{20}O_2$. Computed: MR_D 54.87.

3.880 mg substance: 10.402 mg CO_2; 3.510 mg H_2O.
8.12 mg substance: 21.84 mg CO_2; 7.48 mg H_2O.
Found %: C 73.2, 73.3; H 10.1, 10.3.
$C_{12}H_{20}O_2$. Computed %: C 73.5; H 10.2.

The 2,4-dinitrophenylhydrazone of the methoxyindanone (XV) fused at 98-98.5° after recrystallization from a mixture of petroleum ether and benzene.

3.485 mg substance: 0.500 ml N_2 (23°, 739 mm).
3.675 mg substance: 0.519 ml N_2 (23°, 738 mm).
Found %: N 15.6, 15.8.
$C_{18}H_{24}O_5N_4$. Computed %: N 14.9.

Hydrolysis of 3,8-dimethyl-5-methoxy-Δ^5-tetrahydroindan-1-one. 2 g of the methoxyindanone (V) and 12 ml of 3% hydrochloric acid were shaken together for three hours at room temperature. The organic layer was removed, and the aqueous layer was saturated with ammonium chloride and extracted with ether. The product was distilled in vacuum after the ether had been driven off. This yielded 1.5 g of 3,8-dimethylhydrindan-1,5-dione (XVI) with a b.p. of 101-102° at 0.07 mm; n_D^{20} 1.4928.

4.600 mg substance: 12.334 mg CO_2; 3.740 mg H_2O.
6.450 mg substance: 17.347 mg CO_2; 5.275 mg H_2O.
Found %: C 73.2, 73.4; H 9.1, 9.1.
$C_{11}H_{16}O_2$. Computed %: C 73.4; H 8.9.

The disemicarbazone of the hydrindanone (XVI) is insoluble in organic solvents. It fuses at 234-235° with decomposition after being purified by double boiling with alcohol.

3.610 mg substance: 6.965 mg CO_2; 2.485 mg H_2O.
3.412 mg substance: 6.585 mg CO_2; 2.315 mg H_2O.
Found %: C 52.5, 52.6; H 7.7, 7.6.
$C_{13}H_{22}O_2N_6$. Computed %: C 53.0; H 7.5.
4.690 mg substance: 1.107 ml N_2 (21°, 754 mm).
4.380 mg substance: 1.104 ml N_2 (22°, 753 mm).
Found %: N 27.2, 27.4.
$C_{13}H_{22}O_2N_6$. Computed %: N 28.5.

Condensation of 5-methoxy-3,8-dimethyl-Δ^5-tetrahydroindan-1-one with acetylene. 7.9 g of methoxyindanone (V) and 50 ml of absolute ether were saturated at -70° (chilling with dry ice) with acetylene for 30 minutes. A solution of 11 g of metallic potassium in 90 g of absolute tert-amyl alcohol was added with vigorous stirring and the continued passage of acetylene. Then the acetylene was passed through, with constant stirring, for another 7 hours at -70° and for ten hours the next day at -15 to -30°. The product was treated with 15 ml of water, the aqueous layer was removed and extracted with ether, and the ether-alcohol solution was neutralized by passing carbon dioxide through and then desiccated with magnesium sulfate. The ether and the tert-amyl alcohol were driven off in a slight vacuum, and the residue was distilled at 1 mm:

Fraction 1: b.p. 108-120° at 1 mm; n_D^{20} 1.4940 - 2.9 g,

Fraction 2: b.p. 120-122° at 1 mm; n_D^{20} 1.5175 - 4.3 g.

Fraction 2 is 1-ethynyl-5-methoxy-3,8-dimethyltetrahydroindan-1-ol (VI), a viscous, colorless liquid, which forms a voluminous precipitate with ammoniacal silver nitrate.

6.84 mg substance: 18.85 mg CO_2; 5.58 mg H_2O.
Found %: C 76.3; H 9.3.
$C_{14}H_{20}O_2$. Computed %: C 76.4; H 9.1.

The acetylenic alcohol (VI) was wholly converted into the methyl ether of the keto alcohol (XX) by subsequent repeated fractionation in vacuum of the resulting fractions:

B.p. 104-107° at 2 mm; n_D^{20} 1.4945; d_4^{20} 1.043; MR_D 61.54.
$C_{14}H_{20}O_2$. Computed: MR_D 62.10.

13.69 mg substance: 37.71 mg CO_2; 11.26 mg H_2O.
4.87 mg substance: 13.595 mg CO_2; 4.043 mg H_2O.
Found %: C 76.2, 76.2; H 9.3, 9.3.
$C_{14}H_{20}O_2$. Computed %: C 76.4; H 9.1.
20.104 mg substance: 24.81 ml 0.02N $Na_2S_2O_3$.
Found %: OCH_3 14.16.
$C_{14}H_{20}O_2$. Computed %: OCH_3 14.09.

The methyl ether of the acetylenic keto alcohol (XX) is a mobile, colorless liquid, which forms a curdled precipitate with ammoniacal silver nitrate. Determination of the hydroxyl groups by the Chugayev-Tserevitinov method indicated that there was no active hydrogen in this substance.

The methyl ether of the keto alcohol (XX) does not form a crystalline derivative with semicarbazide acetate; its 2,4-dinitrophenylhydrazone fuses at 111° after recrystallization from alcohol.

3.795 mg substance: 0.461 ml N_2 (21°, 758 mm).
4.150 mg substance: 0.510 ml N_2 (21°, 758 mm).
Found %: N 14.1, 14.2.
$C_{20}H_{27}O_5N_3$. Computed %: N 14.0.

Synthesis of 1-ethynyl-5-keto-3,8-dimethylhexahydroindan-1-ol. 18 g of the methoxyindanone (V) was condensed with acetylene by the method described above. 20 ml of 10% hydrochloric acid was added to the alcohol-ether solution neutralized with carbonic acid, and the mixture was stirred for five hours at room temperature. Then the mixture was neutralized with soda, and the ether, water, and tert-amyl alcohol were driven off in a slight vacuum. White crystals settled out when the solution was cooled. Recrystallization from alcohol yielded 8 g of 1-ethynyl-5-

keto-3,8-dimethylhexahydroindan-1-ol (VII) as colorless lamellae with a m.p. of 135°, which form a voluminous precipitate with ammoniacal silver nitrate.

5.951 mg substance: 16.499 mg CO_2; 4.668 mg H_2O.
4.975 mg substance: 13.855 mg CO_2; 3.950 mg H_2O.
Found %: C 75.7, 75.9; H 8.7, 8.9.
$C_{13}H_{18}O_2$. Computed %: C 75.7; H 8.7.

The semicarbazone of the acetylenic keto alcohol (VII) fused at 188-188.5° after recrystallization from alcohol.

5.040 mg substance: 0.688 ml N_2 (21°, 766 mm).
4.850 mg substance: 0.651 ml N_2 (20°, 766 mm).
Found %: N 16.0, 15.8.
$C_{14}H_{21}O_2N_3$. Computed %: N 16.0

Fractionation of the mother liquor yielded:

Fraction 1: b.p. 122-132° at 2 mm; n_D^{19} 1.4952 - 1.5 g,

Fraction 2: b.p. 145-150° at 2 mm; n_D^{19} 1.5080 - 7 g.

after the acetylenic keto alcohol (VII) had been removed.

Both fractions form a voluminous white precipitate with ammoniacal silver nitrate. Fraction 1 consists chiefly of the methyl ether of acetylenic keto alcohol (XX). Fraction 2 is the acetylenic keto alcohol (VII) with an admixture of its methyl ether (XX).

Selective hydrogenation of 1-ethynyl-5-keto-3,8-dimethyltetrahydroindan-1-ol. 3.88 g of the acetylenic keto alcohol (VII) in a solution of 20 ml of dioxane was hydrogenated with a Pd catalyst. 4.55 ml of hydrogen (1 mol) was absorbed. Driving off the dioxane left white crystals of 1-vinyl-5-keto-3,8-dimethylhexahydroindan-1-ol (VIII) with a m.p. of 70-71° (from alcohol):

4.592 mg substance: 12.679 mg CO_2; 4.049 mg H_2O.
4.655 mg substance: 12.839 mg CO_2; 3.990 mg H_2O.
Found %: C 75.3, 75.2; H 9.7, 9.6.
$C_{13}H_{20}O_2$. Computed %: C 75.0; H 9.6.

The semicarbazone of the vinylic ketoindanol (VIII) fused at 186-187° after recrystallization from alcohol (a sample mixed with the semicarbazone of the acetylenic keto alcohol (VIII) fused at 160-165°).

4.755 mg substance: 0.665 ml N_2 (24°, 755 mm).
4.303 mg substance: 0.600 ml N_2 (24°, 755 mm).
Found %: N 16.0, 15.9.
$C_{14}H_{23}O_2N_3$. Computed %: N 15.9.

Dehydration of 1-vinyl-5-keto-3,8-dimethylhexahydroindan-1-ol. 1.5 g of the vinylic ketoindanol (VIII) and 0.75 g of powdered potassium bisulfate were heated in a small Claisen flask for 40 minutes at a vacuum of 80 mm and at a bath temperature of 120 to 130°. Fractionation yielded 0.8 g of 1-vinyl-3,8-dimethyl-5-keto-Δ^1-hydrindene (IX):

B.p. 105-106° at 3.5 mm; n_D^{20} 1.5070; d_4^{20} 0.9824; MR_D 57.55.
$C_{13}H_{18}O$. Computed: MR_D 56.91.
12.21 mg substance: 36.74 mg CO_2; 10.64 mg H_2O.
17.08 mg substance: 51.35 mg CO_2; 15.18 mg H_2O.
Found %: C 82.1, 82.0; H 9.7, 9.9.
$C_{13}H_{18}O$. Computed %: C 82.1; H 9.5.

The dienone (IX) was recovered as a slightly yellow mobile liquid. The semicarbazone of the dienone (IX) fuses with decomposition at 192-193° after recrystallization from alcohol.

4.485 mg substance: 0.676 ml N_2 (23°, 749 mm)..
4.440 mg substance: 0.686 ml N_2 (24°, 728 mm).
Found %: N 17.1, 17.1. $C_{14}H_{21}ON_3$. Computed %: N 17.0.

Condensation of 1-vinyl-5-keto-3,8-dimethyl-Δ^1-hydrindene (IX) with maleic anhydride. 0.8 g of the dienone (IX), and 0.4 grams of maleic anhydride were heated in a glass ampoule to 120° for two hours. Two days later the product had crystallized. Recrystallization from a mixture of benzene and petroleum ether yielded the anhydride of 9,11-dimethyl-7-ketodecahydrofluorene-1,2-dicarboxylic acid (XI) with a m.p. of 182-183°.

3.502 mg substance: 9.052 mg CO_2; 2.230 mg H_2O.
2.860 mg substance: 9.413 mg CO_2; 1.790 mg H_2O.
Found %: C 70.5, 70.7; H 7.0, 7.0.
$C_{17}H_{20}O_4$. Computed %: C 70.8; H 6.9.

0.3 g of the anhydride (XI) was heated for 2 hours with 2 ml of 3% hydrochloric acid in a flask fitted with a reflux condenser. The acids were neutralized with soda and filtered, and the neutral products were extracted with ether. The aqueous solution of the salt was acidulated with hydrochloric acid (1:3), and the precipitated crystals of 7-keto-9,11-dimethyldecahydrofluorene-1,2-dicarboxylic acid (XIV) were recrystallized twice from water and ethyl alcohol. The air-dried crystals of the acid fuse at 266-268° with decomposition.

4.04 mg substance: 1.2992 ml 0.01 N NaOH.
4.152 mg substance: 1.333 ml 0.01 N NaOH.
Found: M 311, 311.5.
$C_{17}H_{22}O_5$. Computed: M 306.

0.2 g of the anhydride (XI) was boiled for six hours with 3 ml of absolute ethanol. The precipitated crystals of the monoethyl ester of 7-keto-9,11-dimethyldecahydrofluorene-1,2-dicarboxylic acid (XII or XIII) were filtered out and recrystallized from alcohol; they fused at 140-141° after being dried in the exsiccator over calcium chloride.

8.75 mg substance: 21.79 mg CO_2; 6.37 mg H_2O.
Found %: C 68.0; H 8.1.
$C_{19}H_{28}O_5$. Computed %: C 68.3; H 7.8.

Condensation of 1-vinyl-5-keto-3,8-dimethyl-Δ^1-hydrindene (IX) with 1,3-dimethyl-Δ^1-cyclopentenone (IV). 21.5 g of the dienone (IX), 21.5 g of 1,3-dimethyl-Δ^1-cyclopentenone (IV), and 0.1 g of pyrogallol were heated for six hours to 150-160° in a metallic ampoule. Fractionation yielded 20 g of the initial cyclopentenone (IV), 1 g of the initial dienone (IX), and 0.6 g of the steroid diketone (X) as a viscous yellow liquid with a b.p. of 155-160° at 0.03 mm; n_D^{20} 1.5300.

6.788 mg substance: 19.852 mg CO_2; 5.648 mg H_2O.
3.920 mg substance: 11.508 mg CO_2; 3.304 mg H_2O.
Found %: C 80.04, 80.12; H 9.34, 9.43.
$C_{20}H_{28}O_2$. Computed %: C 80.00; H 9.30.

Before analysis, the substance was kept for two days in a vacuum exsiccator over phosphoric anhydride.

The monosemicarbazone of the steroid tetracyclic diketone (X) fused with decomposition at 212-213° after recrystallization from alcohol.

3.635 mg substance: 0.374 ml N_2 (23°, 732 mm).
4.080 mg substance: 0.412 ml N_2 (23°, 735 mm).
Found %: N 11.42, 11.26.
$C_{22}H_{34}O_2N_6$. Computed %: N 11.70.

Synthesis of 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione (XVII). 10 g of 1,3-dimethyl-Δ^1-cyclopentenone, 10 g of glacial acetic acid, and 10 g of powdered selenium dioxide were heated to 120° in a Claisen flask. Within two to three minutes a violent reaction set in, which lasted ten to fifteen minutes. Whenever the boiling of the mixture became too violent, the flask was cooled with water. When the reaction was over, the acetic acid and the small amount of unreacted ketone were driven off in vacuum. Fractionation of the residue in vacuum yielded 5.2 g of the dione (XVII) with a b.p. of 108-111° at 12 mm as a viscous red liquid, which solidified upon cooling (yield = 45%). After recrystallization from a mixture of benzene and petroleum ether the dione (XVII) was recovered as yellow crystals with a m.p. of 66-66.5°, which are readily soluble in ether, benzene, and dioxane and deliquesce when exposed to the air.

4.270 mg substance: 10.630 mg CO_2; 2.400 mg H_2O.
5.340 mg substance: 13.316 mg CO_2; 3.120 mg H_2O.
Found %: C 67.9, 68.0; H 6.3, 6.5.
$C_7H_8O_2$. Computed %: C 67.8; H 6.5.

The mono-2,4-dinitrophenylhydrazone of the diketone (XVII) fused at 184.5-185.5° with decomposition after recrystallization from alcohol.

3.504 mg substance: 0.578 ml N_2 (20°, 751.3 mm).
3.505 mg substance: 0.546 ml N_2 (20°, 754.3 mm).
Found %: N 19.0, 19.0.
$C_{13}H_{12}O_5N_4$. Computed %: N 18.4.

Diene condensation of 2-methoxy-1,3-butadiene with 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione. 0.7 g of the dione (XVII) and 4 g of 2-methoxybutadiene in 10 ml of dioxane were heated with pyrogallol to 120° for three hours in a metallic ampoule. After 1.5 g of the initial methoxybutadiene and the solvent had been driven off, there remained a thick dark mass that did not crystallize from benzene, petroleum ether, dioxane, or alcohol. The residue was agitated for one hour with 5 ml of 3% hydrochloric acid. The lower organic layer was separated, the aqueous solution was saturated with ammonium chloride and extracted with ether, and the combined ether solution was neutralized with a 5% soda solution and desiccated with magnesium sulfate. Fractionation yielded 0.6 g of 3,8-dimethylhydrindan-1,2,5-trione (XIX), with a b.p. of 125-128° at 0.4 mm, as a thick yellow mass with a typical sharp odor, which turned dark and gradually crystallized when left to stand in vacuum over phosphoric anhydride. Recrystallization from N-hexane yielded colorless flat crystals with a m.p. of 128-129°.

12.47 mg substance: 31.02 mg CO_2; 8.39 mg H_2O.
11.26 mg substance: 27.98 mg CO_2; 7.53 mg H_2O.
Found %: C 67.9, 67.8; H 7.5, 7.4.
$C_{11}H_{14}O_3$. Computed %: C 68.0; H 7.3.

The mono-2,4-dinitrophenylhydrazone of the synthesized trione fused at 179.5° after recrystallization from alcohol.

3.235 mg substance: 0.437 ml N_2 (20°, 730 mm).
3.294 mg substance: 0.441 ml N_2 (19°, 728 mm).
Found %: N 15.0, 15.1.
$C_{17}H_{18}O_6N_4$. Computed %: N 15.0.

SUMMARY

The complete synthesis from acetylene of the steroid diketone (X), which is an isomer of 17-methylandrostenedione with a methylcyclopentane B ring, has been performed. A number of the intermediate products have been described.

LITERATURE CITED

[1] I.N.Nazarov and L.D.Bergelson, J.Gen.Chem., 20, 648 (1950).*

[2] Windaus, Ber., 53, 488 (1920); Lieb. Ann. 447, 233 (1926); Lettre, Z. physiol. Chem., 218, 67 (1933); 221, 73 (1933); Prelog, Ruzicka, Meister, Helv. Chim.Acta, 28, 1651 (1945); Tinataro, Kawasaki, J. pharm. Soc., Japan, 56, 167 (1936); ZBl., 1937, 1, 2183.

[3] I.N.Nazarov and I.I.Zaretskaya, Izv. USSR Acad. Sci., Div. Chem. Sci., 65 (1944).

[4] I.N.Nazarov, Z.P.Verkholetova, and L.D.Bergelson, Izv. USSR Acad. Sci., Div. Chem. Sci., 511 (1948).

[5] I.N.Nazarov and M.B.Kuvarzina, Izv. USSR Acad. Sci., Div. Chem. Sci., 599 (1948).

[6] Dykstra, J. Am. Chem. Soc., 57, 2255 (1935).

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THE PROBLEM OF VINYLATING POLYATOMIC ALCOHOLS

EXPERIMENTS ON THE VINYLATION OF MANNITOL

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At the present time the vinyl alkyl ethers are the subject of intensive and many-sided investigation. Readily polymerized, they yield diversified products that find application in the manufacture of synthetic rubber, plastics, lacquers, adhesives, etc., depending upon the reaction conditions employed: catalyst, process temperature, etc. In Germany, polyvinyl methyl, polyvinyl n-butyl, and polyvinyl isobutyl ethers are employed under the general trade name of Igevin; their characteristics are given in the subjoined table.

Polyvinyl ether	Methyl ether (PVM)	Isobutyl ether (PVI or PVJ)	Normal butyl ether (PVN)
Trade name	Igevin M [2], Appretan W.K.	Opannol C [4], Igevin I [2,3], Casal – adhesive solutions	Not used industrially
Properties	Viscous liquid or balsamlike solution in cold water	Tacky, solid. Non-sticky solid. Viscous, tacky liquid.	Soft rubber, adhering under pressure [2,5]. Tacky, viscous liquid [2,5].
Application	For Buna NN 'Latex' as a coating, plasticizer, for textile treatment, for leather treatment	Pressure-sensitive tapes [1,2] (surgical tapes), shoe adhesives, plasticizer, wax modifier	Applications now being worked out. Various adhesives, less sensitive to temperature than PVI

The copolymerization of vinyl alkyl ethers with some unsaturated compounds, and with α,β-ethylenedicarboxylic acids and their esters, acrylic esters, and other compounds, yields a large number of products that are of practical importance.

The copolymerization of vinyl chloride and a small quantity of vinyl isobutyl ether yields a number of products with varying solubility in organic solvents, which have been in commercial use in Germany under the trade name of Viniflex MR 400 [4].

These examples are a clear indication of the great significance of vinyl alkyl ethers at the present time. On the other hand, the attention of research workers has recently been drawn to the unsaturated esters of polyatomic alcohols and carbohydrates as a possible raw material for products produced by polymerization reactions. Nichols, Wrigley, and Janovsky [5] have synthesized a number of allyl and methallyl ethers of polyatomic alcohols and carbohydrates. They also synthesized [6] allyl and methallyl ethers of glucose and starches that are soluble in organic solvents from partially acylated glucose and starches of various origins. Treadway and Janovsky [7] have described acrylic and methacrylic esters of glucose, dextrin, and starch. Haworth, Montgomery, and Wiggins [8] have synthesized the acrylic and methacrylic esters of mannitol, sorbitol, and benzylidene-glucose.

All these authors have pointed out the readiness with which the synthesized ethers and esters are polymerized.

In this connection the vinyl ethers of polyatomic alcohols and carbohydrates are doubtless of interest. Possessing several hydroxyvinyl groups, these vinyl ethers may be polymerized either with one or several vinyl groups, and, by varying the conditions of polymerization, we can secure a number of products, which might be of importance in the production of rubbers, plastics, lacquers, etc.

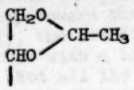
A study of the copolymerization of the vinyl ethers of polyatomic alcohols with vinyl alkyl ethers as well as with dienes might aid in solving the problem of the mechanism of plasticizing the rubbers. Moreover, since vinyl ethers are highly active chemically, they may serve as the initial material for synthesizing many other products.

Favorsky and Shostakovsky [9] have worked out a convenient method for synthesizing vinyl ethers by the direct action of acetylene upon alcohols and phenols in the presence of KOH. The same authors pointed out that the vinylation of ethylene glycol results in the formation of glycol acetal, together with divinyl glycol ether, by the intramolecular addition of a hydroxyl group at the double bond of the monovinyl glycol ether. Subsequently, Shostakovsky and Gershtein [10] showed that with traces of mineral acids present, alcohols add vinyl ether at the double bond, giving rise to an acetal.

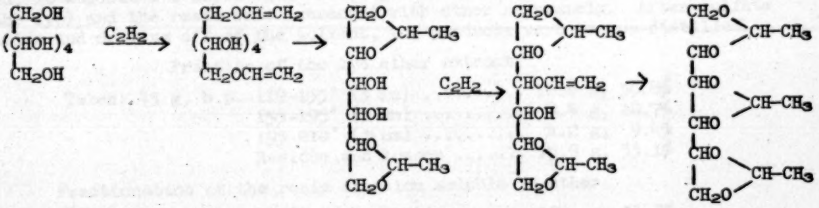
Hennion, Killian, and Nieuwland [11] synthesized a number of ketals by reacting alkyl acteylenes with alcohols in the presence of BF_3 and HgO in an ether solution, finding that the reaction involves the formation of intermediate vinyl alkyl ethers. By reacting organic acids with alkyl acetylenes Hennion and Nieuwland [12] have synthesized a number of vinyl acyl ethers and their corresponding ketoacylals.

It may be expected that the vinylation reaction will be very complicated in the case of polyatomic alcohols, such as mannitol. In the ideal case it might be expected that acetylene would be added to all six hydroxyl groups, giving rise to a hexavinyl ether of mannitol. In actuality, mannitol possesses six hydroxyl groups, which are structurally heterodynamic, and hence the formation of the ethers must take place at different rates. It is well known that complete alkylation of polyatomic alcohols and carbohydrates requires prolonged treatment with a large excess of the alkylating agent (as in methylation, for example). Nichols, Wrigley, and Janovsky [5] synthesized hexaallyl and hexamethallyl mannitols, the process of allylation and methallylation taking place in two stages: in the first stage, the action of $CH_2=CH-CH_2Br$ in the presence of 50% alkali yielded a product that contained four or more methallyl groups; only in the second stage were fully substituted hexaallyl and methallyl ethers obtained by treatment with the corresponding bromide in the presence of metallic sodium.

It is evident that the vinylation of mannitol will also take place with different rates for the individual hydroxyl groups, which is why the formation of cyclic acetal groups is also possible in this instance as follows:



This is borne out by the recovery of a crystalline product, whose elementary analysis indicated it was a trisubstituted product with no active hydrogen, from the vinylation products. This enables us to identify it as triacetalmannitol, which is formed as follows:



The vinylation products are a complex mixture of the products of the mannitol, which contains a small amount of hydroxyvinyl groups in addition to ethylidene groups, evidence of which is the low value of their iodine numbers. The high molecular weight, 472 instead of 338 (computed for hexavinylmannitol), indicates that in vinylation acetalization takes place in several mannitol molecules, two at least, in addition to the formation of cyclic acetal groups.

When the products of mannitol vinylation are distilled, we always get a large quantity of a residue that does not distil in vacuum. When the initial reaction product was extracted with ether, part of it was not extracted by the ether, but was fully extracted by an alcohol-benzene mixture. The alcohol-benzene fraction of the distillation residues was not analyzed further, but it may be assumed that the residues were formed in part as a result of polymerization of the double bonds of the hydroxyvinyl groups and partly as a result of acetalization, giving rise to the formation of compounds of the polyacetal type.

There is every reason to assume that the slight unsaturation of the products analyzed is due to the fact that the resulting polyvinyl ethers of mannitol undergo further polymerization, which makes it impossible to separate them.

Research on vinylation products is being continued.

EXPERIMENTAL

Mannitol was vinylated by a single method. 91 g of mannitol (0.5 mol) was dissolved in 500 ml of 10% KOH, and the solution was placed in a Bergius bomb, into which acetylene was fed from a tank. The bomb was flushed 2 or 3 times with acetylene to clear out the air, after which the bomb was filled and the heat turned on. The initial pressure was 10-12 atm. Since preliminary tests had established that the vinylation reaction is too slow at temperatures of the order of 100-120°, the vinylation tests were made at 140-160°. Whenever the pressure in the bomb dropped

too low, acetylene was added until the initial pressure had been restored.

At the commencement of the test, acetylene was absorbed rapidly, but this absorption slowed down considerably toward the end of the reaction. The experiment lasted about 130 hours. Outwardly, the reaction mixture was a dark, resinous mass; it was extracted with ether together with a light brown aqueous emulsion, which will be henceforth called "lye". Not all the product was extracted, the residue left after ether extraction being extracted with a 2:1 alcohol-benzene solution. This latter extraction was complete. The ether solution was desiccated with calcined sodium sulfate, and the solvent was driven off. This yielded 120 g of a dark-brown product, a thin layer of which was transparent. When a thin layer was allowed to stand, it deposited a solid film on the glass. In some tests, the aqueous emulsion (the lye) and the resin were extracted with ether separately. After sulfate desiccation and driving off of the solvent, the products were vacuum-distilled.

Fraction of the lye ether extract

Taken: 45 g, b.p. 119-155° (3 mm) ..... 16.6 g, 36.8%
155-195° (3 mm) ..... 8.4 g, 18.7%
195-210° (3 mm) ..... 4.2 g, 9.4%
Residue and losses ..... 15.9 g, 35.1%

Fractionation of the resin fraction soluble in ether

Taken: 19.6 g, b.p. 118-150° (3 mm) ..... 10 g, 51.7%
150-195° (3 mm) ..... 3.7 g, 20%
Residue and losses ..... 5.6 g, 28.3%

The low-boiling fractions partially crystallized upon standing and cooling. After the crystals had been filtered out, the liquid was distilled.

Taken for distillation: 25.75 g, b.p. 120-145° (3 mm).... 10.35 g, 40%
146-155° (3 mm).... 10.67 g, 41%
156-160° (3 mm).... 1.8 g, 7%
Residue ..... 2.15 g 8%

The fraction with a b.p. of 120-145° at 3 mm yielded:

0.0888 g substance: 0.1886 g CO_2; 0.0566 g H_2O.
0.0884 g substance: 0.1878 g CO_2; 0.0522 g H_2O.
Found %: C 57.92, 57.94; H 7.14, 7.64.

The fraction with a b.p. of 146-155° at 3 mm yielded:

0.0634 g substance: 0.1320 g CO_2; 0.0396 g H_2O.
0.070 g substance: 0.1460 g CO_2; 0.0432 g H_2O.
Found %: C 57.04, 56.56; H 6.99, 6.90.

The fraction with a b.p. of 156-195° at 3 mm yielded:

0.0722 g substance: 0.1646 g CO_2; 0.0480 g H_2O.
0.0718 g substance: 0.1624 g CO_2; 0.0478 g H_2O.
Found %: C 62.77; 62.06; H 7.43, 7.45.

Iodine number

18.90 for the fraction with a b.p. of 120-145° at 3 mm;
22.63 for the fraction with a b.p. of 146-155° at 3 mm;
27.32 for the fraction with a b.p. of 156-195° at 3 mm;

Distillation of the product at atmospheric pressure yielded the following results: taken 116.7 g; 4.25 g distilled up to 153°; 55.9 g distilled from 153° to

250°; decomposition set in as the temperature was raised still higher.

The 159-250° fraction was repeatedly fractionated, resulting in the recovery of 5.59 g of a light-yellow, mobile oil, which distilled at 243-270°. Chilling with snow yielded 3.46 g of a crystalline product: d_4^{28} 1.1242; n_D^{20} 1.4865.

0.3269 g substance: 19.06 g benzene: Δt 0.190°.
0.1875 g substance: 19.06 g benzene: Δt 0.100°.
Found: M 452, 492.

Outwardly, the crystalline product had the appearance of colorless acicular crystals. Its melting point was 77° (uncorrected) after repeated recrystallization. It is soluble in all organic solvents; the Tserevitinov test was negative.

0.0596 g substance: 0.1200 g CO_2; 0.0380 g H_2O.
0.0662 g substance: 0.1322 g CO_2; 0.0428 g H_2O.
Found %: C 54.91, 54.46; H 7.14, 7.24.
$C_{12}H_{20}O_6$. Computed %: C 55.38; H 7.59.

SUMMARY

1. Vinylation of mannitol yielded a crystalline product, identified as triacetalmannitol, and a liquid product that was a complex mixture of mixed vinyl ethers and acetals of mannitol.

2. The possible reaction mechanism is discussed. Owing to the heterodynamic nature of the hydroxyl groups in the mannitol molecule, their vinylation proceeds at uneven rates under the given conditions, which is why the resulting vinyl ethers of mannitol polymerize at once, forming cycloacetals.

Because of the increased number of hydroxyl groups in mannitol, the formation of cycloacetals is paralled by acetalization involving a binding of some mannitol molecules with an ethylidene group, i.e., the addition of two molecules of mannitol to a molecule of acetylene.

LITERATURE CITED

[1] Muller and Piero, U.S.Patent 2061934; Reppe and Kuhn, U.S.Patent 2098108; Reppe and Schienting, U.S.Patent 2104000.
[2] De B.M.Goggins, A.M.Gloor, Overseas Investigation Team Rept. Appendix 6A, 150-1. Office of Quatermaster Gen., Nov., 1945. Cited in: Schildknecht, Zoss, Clyde, McKinley, Ind. Eng. chem., 39, 2, 180 (1947).
[3] Carothers, Collins, Kirby, U.S.Patent 2066330; Fikentscher, U.S.Patent 2016490; Jourdan, Kollek, Ufer. U.S.Patent 2054019; Voss, Dickhauser, U.S.Patent 20 2047398.
[4] Craemer, Kautschuk, 15, 23 (1939).
[5] Nicholas, Wrigley, Janovsky, J.Am.Chem.Soc., 68, 2020 (1946).
[6] U.S.Patent 2406369.
[7] Treadway, Janovsky, J.Am.Chem.Soc., 67, 1038 (1945).
[8] Haworth, Montgomery, Wiggins, J.Chem.Soc., 1946, 488.
[9] Favorsky and Shostakovsky, J.Gen.Chem. 13, 1 (1943).
[10] Shostakovsky and Gershtein, J.Gen.Chem. 16, 436 (1946).
[11] Hennion, Killian, Nieuwland, J.Am.Chem.Soc., 56, 1130 (1934).
[12] Hennion, Nieuwland, J.Am.Chem.Soc., 56, 1602 (1934).

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THE ISOMERIZATION OF UNSATURATED HYDROCARBONS IN CONTACT WITH METAL OXIDES

IX. THE ISOMERIZATION OF ACETYLENE HYDROCARBONS OVER CHROMIC OXIDE ON ALUMINA

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In our preceding report [1] we described the isomerization of an α-acetylenic hydrocarbon (1-hexyne) above a composite contact agent – chromic oxide on alumina. It was shown that in a single pass over this contact agent at 250°, 1-hexyne undergoes complete conversion into a mixture of isomeric hydrocarbons – hexynes with a lower position of the triple bond (2-hexyne and 3-hexyne) and an alkadiene with conjugated double bonds (2,4-hexadiene).

The present paper discusses the contact isomerization of a β-acetylenic hydrocarbon – 2-hexyne. It was found that the β-acetylenic hydrocarbon undergoes complete isomerization, like the α-acetylenic hydrocarbon, with a shift of the triple bond deeper into the molecule during a single pass over chromic oxide on alumina at 250°, plus the conversion of the triple bond into two double bonds that constitute a conjugated system. The products of the isomerization of 2-hexyne proved to be 3-hexyne and 2,4-hexadiene (dipropenyl).

The presence of dipropenyl in the resulting condensate was demonstrated by producing an addition compound with maleic anhydride; the melting point of this addition compound conformed to the figure given in the literature, and a test sample (with the addition compound formed from pure dipropenyl) exhibited no depression.

Treatment of the condensate with maleic anhydride (without a solvent) yielded another isomerization product, oxidation of which resulted in the formation of nothing but propionic acid, which was identified by the boiling point and melting point of its phenylphenacyl derivative; the results of oxidation allow us to conclude that the second hydrocarbon, a product of the isomerization of 2-hexyne, is 3-hexyne.

Continuing our research on the contact isomerization of acetylenic hydrocarbons, we explored the isomerization of two other isomeric acetylenic hydrocarbons – 1-pentyne and 2-pentyne – above chromic oxide on alumina. By analogy with the isomerization of 1-hexyne previously described by us [1], it might have been expected that the products of the isomerization of 1-pentyne are an acetylenic hydrocarbon with a deeper position of the triple bond (2-pentyne) and the conjugate diene hydrocarbon with the same number of carbon atoms (piperylene).

Experiments have shown that after a single pass of 1-pentyne over chromic oxide on alumina at 250°, the condensate did not contain even a trace of the initial α-acetylenic hydrocarbon (proved by its reaction with silver nitrate) and that it consisted of a mixture of piperylene and 2-pentyne. The presence of piperylene in its trans-form [2] in the condensate was proved by the synthesis of the addition compound with maleic anhydride; the melting point of this addition compound conformed to the figure given in the literature, and a test sample (mixed with the addition compound prepared from piperylene and maleic anhydride) exhibited no depression.

It was found possible to separate the other isomerization product – 2-pentyne – from the piperylene (owing to its high boiling point as compared to that of piperylene) by fractionation into a tower;* its constants conformed to the data in the literature.

The last of the alkynes investigated by us in the present research, 2-pentyne, is of particular interest in that the contact isomerization of this hydrocarbon ought to involve merely the disproportionation of the triple bond into two double bonds, inasmuch as the second process, the shift of the triple bond deeper into the molecule, could not occur.

Experiment has shown that after a single pass of 2-pentyne over chromic oxide on alumina at 250°, the condensate was a mixture of the initial 2-pentyne and a single product of the former's isomerization, a diene hydrocarbon with conjugated double bonds – piperylene, which totaled 50% of the condensate freed from polymers.

EXPERIMENTAL

1. Contact Isomerization of 2-Hexyne

2-Hexyne was synthesized as follows:

$$C_2H_5CH_2C{\equiv}CH \xrightarrow{NaNH_2} C_2H_5CH_2C{\equiv}CNa \xrightarrow{(CH_3)_2SO_4} C_2H_5CH_2C{\equiv}CCH_3$$

1-Pentyne (the synthesis of which is described below) was methylated with dimethyl sulfate [3]. 39 g of 1-pentyne was added drop by drop to 30 g of sodium amide, previously pulverized under absolute ether and covered with the latter. The reaction mixture was then heated over a water bath for 2 hours, and during this heating 96 g of freshly prepared dimethyl sulfate was added to it. After heating for 2 hours the reaction mixture was decomposed with water (with a small addition of ammonia); the ether solution was removed, washed, and desiccated with calcium chloride. After the ether had been driven off (with a 1-meter dephlegmator), fractionation into a tower produced 2-hexyne (60% of the theoretical yield) with the following constants:

B.p. 83.5° (760 mm); n_D^{20} 1.4139; d_4^{20} 0.7401; MR_D 27.71.
C_6H_{10}. Computed: MR_D 28.08.
Literature data: B.p. 84-85°; n_D^{20} 1.4135; d_4^{20} 0.740 [3].

The 2-hexyne (20.5 g) was passed over chromic oxide on alumina** (internal diameter of the tube = 16 mm, length of the contact agent = 40 cm) in a gentle current of nitrogen at 250° and at a rate of 0.12-0.15 ml per minute. The yield of the condensate (16.6 g) was 81% by weight of the initial hydrocarbon. Distillation of the resulting condensate yielded a fraction (13 g, i.e., 65% by weight of the initial hydrocarbon) with a b.p. of 79-84° and n_D^{20} 1.4390. At the boiling point (79-84°), this fraction was a mixture of the initial hydrocarbon (2-hexyne) with the possible

*A tower with an efficiency of 18 theoretical trays was used in this research for distilling acetylenic hydrocarbons.

**The activity of this contact agent was checked prior to each run by isomerizing diallyl above it [4].

product of its isomerization: 3-hexyne; but its refractive index was much higher than that of these latter hydrocarbons. By analogy with the previously explored isomerization of 1-hexyne above this same contact agent it might have been assumed that the product of the isomerization of 2-hexyne also contained dipropenyl (2,4-hexadiene), an isomer of the hexynes but with conjugated double bonds.

In order to prove the presence of dipropenyl, as well as to purify it of the acetylenic hydrocarbons, 8 g of the isomerization product with a b.p. of 79-84° was heated with maleic anhydride (without a solvent). The part of the fraction that did not react with the maleic anhydride was extracted by boiling the reaction mixture repeatedly with ether. Crystals with a m.p. of 93-93.5° were recovered from the solid residue after treatment with hot water (to remove the maleic anhydride) and recrystallization from ligroin. The data in the literature [5] for dimethyltetrahydrophthalic anhydride (the addition product of maleic anhydride and dipropenyl) are: b.p. 95-96°. A test sample mixed with the addition compound prepared from pure dipropenyl, which had a m.p. of 93-94°, exhibited no depression.

Hence, it has been established that the product of the contact isomerization of 2-hexyne contains dipropenyl; judging by the refractive index of the distilled condensate (1.4390), the content of dipropenyl amounted to 67%.* The ether was driven off from the ether extracts, which contained that part of the condensate that did not react with the maleic anhydride; the residue was reheated with maleic anhydride and distilled over it. The hydrocarbon thus isolated (2.8 g, i.e., 35% of the condensate used) possessed the following constants:

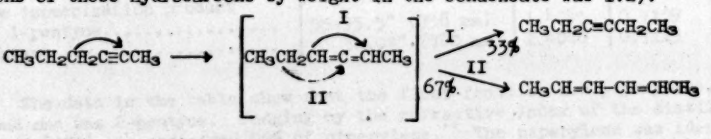
B.p. 80-82° (760 mm); n_D^{20} 1.4170; d_4^{20} 0.7281.
Literature data: b.p. 81° (760 mm); n_D^{20} 1.4115; d_4^{20} 0.7231 [7].

The somewhat higher constants of the resulting acetylenic hydrocarbon indicated that a slight trace of dipropenyl was present. The position of the triple bond in the synthesized hydrocarbon was established by oxidizing it with nitric acid (68%) in the presence of mercuric nitrate [8]. The sole oxidation product proved to be propionic acid with a b.p. of 140-142°, whose phenylphenacyl derivative ($CH_3CH_2COOCH_2COC_6H_4C_6H_5$) had a b.p. of 101°.

A test sample mixed with the phenylphenacyl derivative prepared with pure propionic acid exhibited no depression.

Literature data for propionic acid: Hennaut [9] - b.p. 141.35° (760); Drake [10] - m.p. of its phenylphenacyl derivative 102°.

Hence, 2-hexyne, when in contact with chromic oxide on alumina at 250°, undergoes complete isomerization, giving rise to 3-hexyne and 2,4-hexadiene (the proportions of these hydrocarbons by weight in the condensate was 1:2):



2. Contact Isomerization of 1-Pentyne

1-Pentyne was synthesized by the usual method employed for the synthesis of α-acetylenic hydrocarbons:

*In computing the percentage of dipropenyl in the condensate, we took the refractive index of dipropenyl to be 1.4512 [6] and that of 3-hexyne to be 1.4115 [7].

$$C_2H_5MgBr + CH_2{=}CH{-}CH_2Cl \longrightarrow C_2H_5CH_2CH{=}CH_2 \xrightarrow{+\,Br_2} C_2H_5CH_2\,CHBrCH_2Br \xrightarrow{\downarrow} C_2H_5CH_2C{\equiv}CH$$

Two molecules of hydrogen bromide were split off from 1,2-dibromopentane [b.p. 58-60° (10-11 mm); n_D^{20} 1.5088; d_4^{20} 1.6708; MR_D 41.07; computed MR_D 40.8] by sodium amide [3] in a kerosene solution* at 160-170°.

After having been heated for 6 hours, the reaction mixture was decomposed with water, and the kerosene layer was removed, washed with water until its reaction was neutral, and desiccated with calcium chloride. The 1-pentyne was driven off from the desiccated kerosene layer with a 1-meter dephlegmator. The output totaled 36% of the theoretical. The 1-pentyne possessed the following constants after redistillation into a tower:

B.p. 39.7° (756 mm); n_D^{20} 1.3859; d_4^{20} 0.6931; MR_D 23.06.
C_5H_8. Computed: MR_D 23.10.
Literature data: B.p. 40.25° (760 mm); n_D^{20} 1.3852; d_4^{20} 0.6908. [11]

19 g of 1-pentyne was passed over chromic oxide on alumina under conditions like those described above (at 250° and at a rate of 0.12-0.15 ml per minute). The output of the condensate (14 g) totaled 73% by weight of the 1-pentyne used. The distilled condensate (11 g, 58% of the initial hydrocarbon) had a b.p. of 41-57° (757 mm) and n_D^{20} 1.4172; it contained not a trace of the initial 1-pentyne (it caused no precipitate, nor even cloudiness, when reacted with ammoniacal silver nitrate).

Inasmuch as the possible products of the isomerization of 1-pentyne: piperylene (1,3-pentadiene) and 2-pentyne, have different boiling points, an endeavor could be made to separate them by fractionating the condensate. Double fractionation into a tower yielded two fractions (4 g each), the constants of which are listed in the subjoined table; the data in the literature for piperylene and 2-pentyne are given in the same table for the sake of comparison.

Hydrocarbon	Boiling point	n_D^{20}	d_4^{20}	Reference
First fraction recovered from the isomerization product of 1-pentyne	40.5-42° (738 mm)	1.4269	0.6904	–
Piperylene	40.5-42° (760 mm)	1.4258	0.6907	[12]
Second fraction recovered from the isomerization product of 1-pentyne	55-55.5° (738 mm)	1.4043	0.7139	–
2-Pentyne	56.07° (760 mm)	1.4040	0.7115	[13]

The data in the table show that the first fraction was piperylene, while the second one was 2-pentyne. Judging by the refractive index of the distilled condensate (1.4172), it contained 50% of piperylene.** The piperylene was identified by its addition compound with maleic anhydride. Part of the first fraction was heated with maleic anhydride in the presence of picric acid [2]. Double recrystallization of the

*The kerosene (190-240° fraction) was first treated with sulfuric acid, washed until its reaction was neutral, desiccated with calcium chloride, and distilled over metallic sodium.

**In computing the percentage of piperylene in the condensate we took the refractive index of trans-piperylene as 1.4300[2], and that of 2-pentyne as 1.4040 [13].

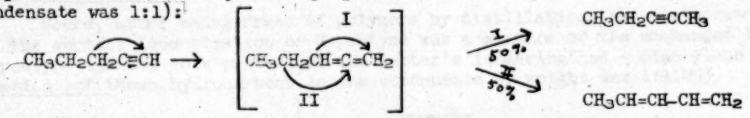
reaction product from ligroin yielded crystals with a m.p. of 59°. Analysis of the addition compound indicated its composition to be $C_9H_{10}O_3$.

5.105 mg substance: 12.115 mg CO_2; 2.900 mg H_2O.
4.335 mg substance: 10.275 mg CO_2; 2.490 mg H_2O.
Found %: C 64.69, 64.67; H 6.36, 6.43.
$C_9H_{10}O_3$. Computed %: C 65.04; H 6.10.

A test sample mixed with the addition product prepared from pure piperylene, which had a m.p. of 60°, exhibited no depression.

Literature data on the addition product of trans-piperylene* and maleic anhydride: Frank [2] – m.p. 61°.

Hence, 1-pentyne in contact with chromic oxide on alumina at 250° undergoes complete isomerization, forming 2-pentyne, identified by its characteristic constants, and piperylene (1,3-pentadiene), identified by its constants and its addition compound with maleic anhydride (proportion of these hydrocarbons by weight in the condensate was 1:1):



3. Contact Isomerization of 2-Pentyne

The 2-pentyne was synthesized as follows:

$$CH_3CH_2CHBrCH_2Br \xrightarrow{-2HBr} CH_3CH_2C{\equiv}CH \xrightarrow{NaNH_2} CH_3CH_2C{\equiv}CNa \xrightarrow{(CH_3)_2SO_4} CH_3CH_2C{\equiv}CCH_3.$$

The two molecules of hydrogen bromide were detached from the 1,2-dibromobutane [b.p. 60-62° (13 mm); n_D^{20} 1.5128; d_4^{20} 1.7998; MR_D 35.83; computed 36.02] by sodium amide in a kerosene solution at 150-160°. After 6 hours of heating, the reaction mixture was decomposed with water; the 1-butyne that separated out was desiccated with calcium chloride and condensed in a receiver chilled with a snow-salt mixture. The resulting 1-butyne was added** to the sodium amide in absolute ether (the sodium amide had been previously pulverized under ether) with constant stirring. The reaction mixture was then stirred for another 2 hours, after which dimethyl sulfate was gradually added to it (with heating), and the whole was heated for 3 hours. After the reaction mixture had been decomposed with water (with a slight quantity of ammonia added), the ether layer was removed and desiccated with calcium chloride. The ether was driven off with a tall dephlegmator, and the residue was distilled into a tower. The resulting 2-pentyne (40% of the theoretical yield) possessed the following constants:

B.p. 55.5-56.5° (762 mm); n_D^{20} 1.4025; d_4^{20} 0.7101; MR_D 23.36.
$C_5H_8{\equiv}$. Computed: MR_D 23.44.

Literature data for 2-pentyne cited in the foregoing table.

10 g of 2-pentyne was passed over chromic oxide on alumina under the conditions specified above. The output of condensate (6 g) was 60% by weight of the initial hydrocarbon. The condensate, driven off from the polymers (5 g, or 50% by weight of the initial 2-pentyne) had a n_D^{20} 1.4180. Subsequent fractionation into a tower

*As has been established in the paper by Frank [2], only the trans form of piperylene reacts with maleic anhydride.

**The dropping funnel was fitted with a jacket to chill the 1-butyne.

yielded two fractions with the following constants:

1) B.p. 40-43° (759 mm); n_D^{20} 1.4238; d_4^{20} 0.6942 (2.6 g);

2) B.p. 55.5-56° (759 mm); n_D^{20} 1.4062; d_4^{20} 0.7129 (1.3 g).

The constants of the second fraction corresponded to the data in the literature cited above for 2-pentyne [13]; the refractive index of the first fraction was lower that that of trans-piperylene [2]; this is due to the presence of some 2-pentyne in this fraction. Judging by the refractive index of the condensate after it had been freed from polymers, it contained 56% of piperylene. The first fraction was condensed with maleic anhydride to identify the piperylene [2]. Double recrystallization from ligroin yielded crystals with a m.p. of 60°. A test sample mixed with the addition compound synthesized with pure piperylene, which had a m.p. of 60°, exhibited no depression. The data in the literature for the addition compound of trans-piperylene with maleic anhydride are cited above.

Hence, after being freed of polymers by distillation, the condensate secured by the contact isomerization of 2-pentyne was a mixture of the unchanged initial 2-pentyne and the sole product of the latter's isomerization - piperylene (the proportion of these hydrocarbons in the condensate by weight was 1:1.25).

SUMMARY

1. A study has been made of the contact isomerization of α- and β-acetylenic hydrocarbons (1-pentyne, 2-pentyne, and 2-hexyne) above a composite contact agent: chromic oxide on alumina.

2. It has been established that 1-pentyne, an α-acetylenic hydrocarbon with a straight chain of carbon atoms, undergoes complete, thoroughgoing isomerization in a single pass over chromic oxide on alumina at 250°, i.e., its triple bond is converted into two double bonds that constitute a conjugated system (50%) and its triple bond is shifted deeper in the molecule (50%).

3. It has been established that the β-acetylenic hydrocarbon, 2-pentyne, undergoes isomerization above the same contact agent and under the same conditions in the only way possible for this compound: the formation of a conjugated alkadiene: piperylene (56%).

4. It has been established that the β-acetylenic hydrocarbon 2-hexyne, the isomerization of which, owing to its structure, may follow two patterns that are typical of the isomerization of α-acetylenic hydrocarbons, undergoes complete isomerization, with a shift of the triple bond deep into the molecule and a conversion of the triple bond into conjugated double bonds, i.e., the formation of 3-hexyne (33%) and 2,4-hexadiene (67%).

5. The contact isomerization of acetylenic hydrocarbons involves the formation of considerable quantity of polymers.

LITERATURE CITED

[1] R.Ya. Levina, E.A.Viktorova, and V.I.Eikhfeld, J.Gen.Chem., 19, 305 (1949).

[2] R.Frank, R.Emmick, R.Johnson, J.Am.Soc., 69, 2313 (1947).

[3] M.Bourguel, Ann. Chim., (10), 3, 222 (1925).

Cf CB translation p. 265 ff.

[4] R.Ya. Levina, Derendyayeva, and A.A.Fainzilberg, J.Gen.Chem. 16, 817 (1946).
[5] O.Diels, K.Alder, Lieb. Ann., 470, 102 (1929).
[6] R.Ya.Levina and P.Ya.Kiryushov, J.Gen.Chem. 9, 1834 (1939).
[7] K.Campbell, L.Eby, J.Am.Chem.Soc., 63, 2683 (1941).
[8] E.Bried, G.Hennion, J.Am.Chem.Soc., 60, 1717 (1938).
[9] Hennaut-Roland, J.Chem.phys., 27, 426 (1930).
[10] W.Drake, J.Bronitsky, J.Am.Soc., 52, 3719 (1930).
[11] F.Morehouse, O.Maas, Can. J. Research, 11, 640 (1934).
[12] E.Grishkevich-Trokhimovsky, J.Russ.Chem.Soc., 48, 880 (1916).
[13] L. Sherril, J.Am.Soc., 60, 2562 (1938).

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THE SYNTHESIS OF HYDROCARBONS

X. THE PARTIAL REDUCTION OF DIENE HYDROCARBONS WITH CONJUGATED DOUBLE BONDS BY SODIUM IN LIQUID AMMONIA

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Our previous reports [1,2] described a new method of synthesizing trans-alkenes with centrally located double bonds. The starting materials used in these syntheses were 1,4-dichlorides of the alkadienes with conjugated double bonds (divinyl and dipropenyl 1,4-dichlorides); these unsaturated dichlorides were reacted with organomagnesium compounds:

$$RCH{=}CH{-}CH{=}CHR \xrightarrow{+\,Cl_2} RCHCH{=}CHCHR \xrightarrow{+\,2R'MgBr} RCHCH{=}CHCHR$$
$$\qquad\qquad\qquad\qquad\quad Cl \qquad Cl \qquad\qquad\qquad\qquad\quad R' \qquad R'$$

(where R = H or CH_3; R' = Alk).

Another possible synthesis of alkenes with centrally located double bonds, based upon the readily available symmetrically constructed alkadienes, presented itself to us in the partial reduction of the latter (at the 1,4-position) by a solution of sodium in liquid ammonia:

$$RCH{=}CH{-}CH{=}CHR \xrightarrow{+\,H_2} RCH_2CH{=}CHCH_2R.$$

Midgley and Henne [3] employed a solution of sodium in liquid ammonia to reduce isoprene. The authors assert that hydrogen was added at the 1,4-position and that they secured a 60% yield of 2-methyl-2-butene, together with some polymeric hydrocarbons, the nature of which was not determined.

Huckel and Bretschneider [4] investigated the reduction by sodium in liquid ammonia of a hydrocarbon that polymerizes readily under these conditions – divinyl. They found that the reaction products were butene and octadiene.

The present paper is a study of the partial reduction of dipropenyl by a solution of sodium in liquid ammonia; this is a symmetrically constructed diene hydrocarbon with conjugated double bond, which is not polymerized under these reaction conditions. Examination of the Raman spectrum of the reduction product indicated

that, contrary to the assertions in the literature cited above, the addition of hydrogen to the diene hydrocarbon does not take place only at the 1,4-position, but predominantly at the 1,2-position, resulting in the formation of a mixture of alkenes with variously located double bonds.

The partial reduction of dipropenyl (2,4-hexadiene) resulted in a mixture of 2-hexene (60-65%) and 3-hexene (35-40%), with both the cis (30%) and the trans (70%) configurations:

Thus, the partial reduction of symmetrical conjugated alkadienes by sodium in liquid ammonia could not be worked up into a preparative method for synthesizing alkenes with centrally located double bonds. This research has, however, enabled us to shed new light on this reaction.

EXPERIMENTAL

1. Partial Reduction of Dipropenyl (2,4-Hexadiene) by Sodium in Liquid Ammonia

An ethereal solution of dipropenyl (16 g) was added with constant stirring to a solution of 36 g of sodium in 250 ml of liquid ammonia chilled to -50 to -60° (by dry ice in alcohol). Stirring was continued for 5-6 hours at the same temperature after all the dipropenyl had been added, and then 100 ml of absolute ether was added and the reaction mass was left to stand overnight at room temperature to drive off the ammonia. The next day the excess sodium was eliminated by adding water (under ether). After the ether had been driven off (into a 1-meter dephlegmator) from the ether extract, which had been washed until its reaction was neutral and then desiccated with calcium chloride, distillation of the reaction product over sodium (into a tower) yielded a hydrocarbon fraction with a b.p. of 67-67.5°, totaling 12 g (75% of the theoretical).

This hydrocarbon fraction (first treated with maleic anhydride to eliminate a any traces of the dipropenyl) was redistilled above sodium into a tower (with 30 theoretical trays); its constants were as follows:

B.p. 67-67.5° (761 mm); n_D^{20} 1.3962; d_4^{20} 0.6802; MR_D 29.74.
C_6H_{12}. Computed: MR_D 29.44.

4.500 mg substance: 14.103 mg CO_2; 5.803 mg H_2O.
4.350 mg substance: 13.645 mg CO_2; 5.612 mg H_2O.
Found %: C 85.49, 85.47; H 14.35, 14.28.
C_6H_{12}. Computed %: C 85.52; H 14.48.

Literature data for 2-hexene and 3-hexene are given in Table 1.

Owing to the closeness of the boiling points of the possible products of the reduction of dipropenyl (at the 1,2- and 1,4-positions); 2-hexene and 3-hexene (67.5-67.7° and 66.9-67.4°, respectively), it is practically impossible to separate them by distillation, and hence the problem of the structure of the reduction products of dipropenyl could be resolved more accurately by an investigation of their combined light-scattering spectra than in any other manner. This optical research also enabled us to solve the problem of the steric structure (cis or trans) of the resulting alkene (or alkenes).

TABLE 1

Hydrocarbon	Boiling point at 760 mm	n_D^{20}	d_4^{20}	References
2-Hexene	67.9-68.1°	1.3928	0.6813	[6]
cis-2-Hexene.....	68.25	1.3952	0.6844	[5]
trans-2-Hexene.....	67.55	1.3934	0.6780	[5]
3-Hexene	66.6-67	1.3942	0.6816	[6]
cis-3-Hexene.....	66.8-66.9 (751 mm)	1.39338	0.67967	[5]
trans-3-Hexene.....	67.4-67.6 (741 mm)	1.3937	0.67782	[5]
cis-3-Hexene.....	66.85-67.15	1.3930	0.6780	[7]
trans-3-Hexene.....	66.4-66.7	1.3943	0.6794	[7]

The complete combined light-scattering spectrum of 3-hexene has been described in one of our previous reports [1]. Inasmuch as the complete spectrum of 2-hexene has not been published in the literature, we had to synthesize this hydrocarbon.

2. Synthesis of 2-Hexene

2-Hexene was synthesized by the action of divinyl hydrochloride upon ethylmagnesium bromide :

$$CH_3CH{=}CHCH_2Cl + C_2H_5MgBr \longrightarrow CH_3CH{=}CHCH_2CH_2CH_3.$$

The divinyl hydrochlorides were prepared by the reaction of (liquid) divinyl with hydrochloride acid [8]. The two allylic isomers $CH_3CH{=}CHCH_2Cl \rightleftarrows CH_3CHClCH{=}CH_2$ were separated and found to have the following constants:

1-Chloro-2-butene: b.p. 84° (748 mm); n_D^{20} 1.4350; d_4^{20} 0.9282; MR_D 25.45. C_4H_7Cl. Computed: MR_D 25.07.

3-Chloro-1-butene: b.p. 64° (748 mm); n_D^{20} 1.4150; d_4^{20} 0.8990; MR_D 25.22. C_4H_7Cl. Computed: MR_D 25.07.

Literature data: 1-chloro-2-butene (Henne and his co-workers [8]: b.p. 83°; n_D^{20} 1.4352; d_4^{20} 0.9316; 3-chlor-1-butene [8]: b.p. 63°; n_D^{20} 1.4153; d_4^{20} 0.9001.

Each of these hydrocarbons and a mixture of the two (a broad fraction) was reacted with ethylmagnesium bromide in separate experiments. But the reaction products were found to be identical in all three cases. Risseghem [9] performed a similar reaction, using divinyl hydrobromide.

One of the experiments is described below. An ethereal solution of 91 g of divinyl hydrochloride was added, with constant stirring, to ethylmagnesium bromide (109 g of ethyl bromide and 24 g of magnesium). After all the hydrochloride had been added, the reaction mass was stirred for 12 hours at room temperature. Decomposition was effected with 10% acetic acid. The ethereal solution of the reaction product was washed until its reaction was neutral and desiccated with calcium chloride and then treated with a solution of sodium in liquid ammonia (prepared with 14 g of sodium and 250 ml of ammonia) to eliminate traces of the halogen. After the customary treatment of the reaction mixture and driving off of the ether (with a 1-meter dephlegmator), the synthesized hydrocarbon was distilled over sodium into a tower (with 30 theoretical trays). This yielded 14 g (17% of the theoretical) of 2-hexene, possessing the following constants:

B.p. 67.5-67.7° (748.5 mm); n_D^{20} 1.3940; d_4^{20} 0.6805; MR_D 29.58. C_6H_{12}. Computed MR_D 29.44.

Literature data for 2-hexene are cited in Table 1.

3. Optical Analysis of 2-Hexene and the Hexene That Is a Product of the Reduction of Dipropenyl

The Raman spectra were recorded with a Steinheil triple-prism glass spectrograph with a mean linear dispersion of ~0.08 mm/A in the 4358-4916 A region. The light source consisted of three IGAR-2 mercury-arc lamps. The 4358 A line was used for excitation. A solution of potassium nitrite was used as the light filter. The frequencies were measured by means of a standard spectrum of an iron arc, recorded with a Hartmann diaphragm. The precision of measurement of the frequencies was ~2.4 cm^{-1}. The intensity of the spectrum lines was evaluated visually. Table 2 gives the frequencies and intensities of the Raman spectra of the hexene produced by the reduction of dipropenyl by sodium in liquid ammonia (I) and the 2-hexene prepared from divinyl hydrochloride and ethylmagnesium bromide (II), as well as the frequencies and intensities of the spectrum of 3-hexene previously synthesized by us from divinyl dichloride and methylmagnesium bromide (III) [1] and the data in the literature for 2-hexene, both for the sake of comparison.

The spectrum of the hexene produced by reducing dipropenyl by sodium in liquid ammonia (I) has two intensive frequencies: 1656 cm^{-1} and 1672 cm^{-1}, which are the characteristic frequencies for the cis and trans forms of the alkenes. The ratio of the intensities of these characteristic frequencies is 13:32. Thus, the hexene examined was a mixture of two steric isomers, with the trans form predominating: ~ 30% of the cis form and ~ 70% of the trans form.

The 2-hexene synthesized by us from divinyl hydrochloride and ethylmagnesium bromide (II), for which the intensity ratio of the characteristic frequencies for the cis and trans forms (1659 cm^{-1} and 1670 cm^{-1}, respectively) was 2:9, likewise is a mixture of the cis form (~ 18%) and the trans form (~ 82%).

The spectrum of the hexene prepared by reducing dipropenyl by sodium in liquid ammonia (I) contains frequencies of average intensity (333, 388, 444, 494, 529, 590, 861, 1096, and 1213 cm^{-1}) that are quite like the frequencies of the spectrum of the 2-hexene prepared from divinyl dichloride and ethylmagnesium bromide (II).

Moreover, the spectrum of the hexene produced by reducing dipropenyl (I) contains frequencies of average intensity (406, 570, 827, 1002, and 1070 cm^{-1}) that are absent in the spectrum of the 2-hexene but are, however, present in the spectrum of the 3-hexene (III). It follows from a comparison of the intensity of these frequencies that the hexene produced by the reduction of dipropenyl (I) consisted of a mixture of 2-hexene (~60-65%) and 3-hexene (~35-40%) in their cis and trans forms.

Thus, when dipropenyl was reduced with sodium in liquid ammonia, the addition of hydrogen to the conjugated system took place at the 1,4-position as well as (in the main) at the 1,2-position.

It should be noted that the process of reducing alkadienes with conjugated double bonds by sodium in liquid ammonia differs fundamentally from the reduction of alkynes with the triple bond in various positions by the same reagent. Whereas trans alkenes with the same position of the double bond are the sole products of the partial reduction of alkynes by sodium in liquid ammonia (and this reaction is an excellent preparative method of synthesizing trans alkenes [11,5]), the reduction of alkadienes by sodium in liquid ammonia results in the production of a mixture of cis and trans alkenes.

The catalytic reduction of hydrocarbons of these two classes – conjugated alkadienes and alkynes – in the presence of Raney nickel differs in the same way: whereas cis alkenes with the same position of the double bond are the sole products of the

TABLE 2

Spectrum of the hexene produced by the reduction of dipropenyl (I)		Spectrum of the hexene prepared from divinyl hydrochloride and ethylmagnesium bromide (II)		Spectrum of 2-hexene according to Hibben [10]		Spectrum of the 3-hexene prepared from divinyl dichloride and methylmagnesium bromide [1] (III)	
Frequency	Intensity*	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
252	3.5	–	–	–	–	221	0.4
276	2	–	–	–	–	–	–
–	–	293	0.5	–	–	–	–
333	3.5	329	1	–	–	–	–
388	3.9	388	4	389	2	–	–
406	0.6	–	–	–	–	406	2; B
444	1.5	446	1.2	–	–	470	2
494	3.5	494	2.5;B	–	–	–	–
529	1.5	529	2	–	–	–	–
570	1	–	–	–	–	567	1.2
590	1.2	587	0.5	–	–	–	–
–	–	693	0.8	–	–	–	–
–	–	–	–	–	–	718	0.2
746	1.5	–	–	–	–	746	0.2
769	2	769	2;B;b	–	–	769	0.2
–	–	792	1	–	–	–	–
827	0.7	–	–	–	–	824	2.8;B;b
–	–	–	–	–	–	839	2.4
861	1.2	857	2.5	857	2	–	–
–	–	–	–	–	–	875	1.6
892	6	890	3	892	2	897	2.8
912	1.2	910	0.5	–	–	–	–
995	2.5	963	0	–	–	–	–
1002	2	–	–	–	–	1002	6
–	–	1015	1.5;b	–	–	–	–
1040	3.2	1040	2.5;B	1040	2	1040	1.2
1070	3.5	–	–	–	–	1068	6
1096	2.5	1091	2.5;B	1095	5	–	–
–	–	–	–	–	–	1107	0.2
1157-1170	1.8;B	1151	1	–	–	1165	0.8
1196	0.6	–	–	–	–	1202	1.2
1213	1.8	1219	1;B	1216	1	–	–
1258	6.5	1256	3.5;B	1258	5	1258	8;B
–	–	–	–	–	–	1296	0.4
1305	10	1305	8.5;B	1308	7	1304	10
–	–	1334	0.5	–	–	1353	0.2
1382	6	1382	3	1378	5	1376	1.2
1440-1460	10;B	1451	10;B	1445	7	1442-60	10;B
1571	1.8	–	–	–	–	–	–
1656	13	1659	4	1658	5	1660	4
1672	32	1670	18	1674	7	1672	40

*B - wide band
b - background

partial reduction of alkynes by the catalytic process (and this reaction is a preparative method for synthesizing the cis alkenes [5,12]), the catalytic reduction of the alkdienes results in the formation of a mixture of cis and trans alkenes [13].

SUMMARY

1. The partial reduction of a symmetrical alkadiene with conjugated double bonds, dipropenyl, by sodium in liquid ammonia has been explored for the first time.

2. It has been established that when dipropenyl is reduced by sodium in liquid ammonia, hydrogen is added both at the 1,2- and the 1,4-positions, resulting in the formation of a mixture of 2-hexene (~60-65%) and 3-hexene (~35-40%), possessing both the cis (~30%) and the trans (~70%) configurations.

3. The reaction of divinyl hydrochloride with ethylmagnesium bromide resulted in the synthesis of 2-hexene (~18% of the cis form and ~82% of the trans form); its Raman spectrum has been investigated.

LITERATURE CITED

[1] R.Ya.Levina, V.R.Skvarchenko, Yu.B.Kagan, and E.G.Treshchova, J.Gen.Chem., 19, 62 (1949).*

[2] R.Ya.Levina, V.R.Skvarchenko, and E.G.Treshchova, J.Gen.Chem., 20, 445 (1950).**

[3] T.Midgley, A.Henne, J.Am.Chem.Soc., 51, 1293 (1929).

[4] W.Huckel, H.Bretschneider, Lieb.Ann., 540, 157 (1938).

[5] K.Campbell, L.Eby, J.Am.Chem.Soc., 63, 216, 2683 (1941).

[6] C.Schmidt, C.Boord, J.Am.Chem.Soc., 54, 751 (1932).

[7] Carr, Walker, J.Chem.phys., 4, 751 (1936).

[8] A.Henne, H.Chanan, A.Turk, J.Am.Chem.Soc., 63, 3474 (1941).

[9] H.Risseghem, Bull.Belg., 47, 47 (1938).

[10] J.Hibben. The Raman Effect and Its Chemical Application. New York, 1939.

[11] A.Henne, K.Grenlee, J.Am.Chem.Soc., 65, 2020 (1943).

[12] K.Campbell, M.O'Conner, J.Am.Chem.Soc., 61, 2897 (1939).

[13] W.Young et.al., J.Am.Chem.Soc., 69, 2046 (1947).

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*See CB translation p. 55 ff.

**See CB translation p. 469 ff.

THE SYNTHESIS OF HYDROCARBONS

XI. THE PARTIAL REDUCTION OF DIENE HYDROCARBONS WITH CONJUGATED DOUBLE BONDS BY SODIUM IN LIQUID AMMONIA

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In our preceding report [1] we described the partial reduction of dipropenyl (2,4-hexadiene) by sodium in liquid ammonia. It was found that the hydrogen is added to the dipropenyl simultaneously at the 1,2- and 1,4-positions, resulting in the formation of a mixture of 2-hexene (~60-65%) and 3-hexene (~35-40%), possessing both cis and trans configurations:

$$CH_3CH{=}CH{-}CH{=}CHCH_3 \rightarrow CH_3CH_2CH{=}CHCH_2CH_3 + CH_3CH{=}CHCH_2CH_2CH_3.$$

The present paper deals with the partial reduction by sodium in liquid ammonia of diisocrotyl (2,5-dimethyl-2,4-hexadiene), a symmetrical alkadiene with conjugated double bonds, which (like dipropenyl) does not polymerize under the given reaction conditions.

Examination of the Raman spectrum of the synthesized hydrocarbon (a yield of 73% of the theoretical), as well as analysis of its oxidation products, indicated that hydrogen is added to diisocrotyl at the 1,2-position when the latter is reduced by sodium in liquid ammonia, resulting in the formation of 2,5-dimethyl-2-hexene, a hydrocarbon that does not possess a centrally located double bond:

$$CH_3C(CH_3){=}CH{-}CH{=}C(CH_3)CH_3 \xrightarrow{+H_2} CH_3CH(CH_3)CH_2CH{=}C(CH_3)CH_3$$

EXPERIMENTAL

1. Synthesis of Diisocrotyl by the Contact Isomerization of Diisobutenyl Above Cromic Oxide on Alumina

The diisobutenyl (2,5-dimethyl-1,5-hexadiene) synthesized by the action of magnesium upon methallyl chloride possessed the following constants:

B.p. 113-114° (755 mm); n_D^{20} 1.4303; d_4^{20} 0.7505; MR_D 37.92.
$C_8H_{14}F_2$. Computed: MR_D 38.21.

This was effected over chromic oxide on alumina* at 250° in a gentle current of nitrogen at a rate of 0.15 ml per minute. Isomerization was effected in a tube with an internal diameter of 17 mm and a contact-agent layer 70 cm long. The catalyst was activated by heating it to 450° in a stream of air after every passage of 20 g of diisobutenyl over it. The condensate had a n_D^{20} 1.4700, i.e., it contained 81% of diisocrotyl (2,5-dimethyl-2,4-hexadiene); the condensate yield was 83% by weight of the diisobutenyl used.

Distillation over sodium into a tower (with 30 theoretical trays) yielded diisocrotyl with the following constants:

B.p. 134-134.5° (747 mm); n_D^{20} 1.4760; d_4^{20} 0.7636; MR_D 40.63.
$C_8H_{14}F_2$. Computed: MR_D 38.21; EM_D 2.42.

Literature data: Prevost [3] – b.p. 134.6° (750 mm); $n_D^{19.5}$ 1.4795; d_4^{20} 0.7646; Henne and Chanan [4] – b.p. 134.5°; n_D^{20} 1.4781; d_4^{20} 0.7615.

2. Partial Reduction of Diisocrotyl (2,5-Dimethyl-2,4-hexadiene) by Sodium in Liquid Ammonia

An ether solution of 15 g of diisocrotyl was added, with constant stirring and with chilling to -50 to -60° (by dry ice in alcohol), to a solution of 24 g of sodium in 250 ml of liquid ammonia.** After all the diisocrotyl had been added, stirring was continued for 5 to 6 hours with chilling, then 100 ml of absolute ether was added, and the reaction mass was allowed to stand overnight at room temperature to evaporate the ammonia. The next day the excess sodium was removed by adding water (under ether). After the ether extract had been washed until its reaction was neutral and then desiccated with calcium chloride, the ether was driven off and the residue was distilled over metallic sodium into a tower (with 30 theoretical trays). This yielded 11 g of a hydrocarbon (73% of the theoretical yield) possessing the following constants:

B.p. 111.2-111.5° (747 mm); n_D^{20} 1.4120; d_4^{20} 0.7182; MR_D 38.83.
$C_8H_{16}F$. Computed: MR_D 38.67.

1.978 mg substance: 6.218 mg CO_2; 2.510 mg H_2O.
4.710 mg substance: 14.510 mg CO_2; 5.980 mg H_2O.
Found %: C 85.74, 85.76; H 14.2, 14.21.
C_8H_{16}. Computed %: C 85.71; H 14.28.

Ozonation. The hydrocarbon was ozonated to determine the position of its double bond. A 6% current of ozone was passed through a solution of 2.5 g of the hydrocarbon in chloroform for 4 hours. After the solvent had been driven off in vacuum, the ozonides were decomposed by heating for a long time with water in the presence of hydrogen peroxide. White crystals with a m.p. of 130.5-131.5° collected in the reflux condenser; this m.p. corresponds to the figure given in the literature for acetone peroxide (Bayer and Villiger [5] – acetone peroxide has a m.p. of 132-133° and is extremely volatile with steam). All the acid recovered from the aqueous solution after the customary treatment distilled at 174°.

4.950 mg substance: 10.625 mg CO_2; 4.225 mg H_2O.
4.370 mg substance: 9.403 mg CO_2; 3.735 mg H_2O.
Found %: C 58.57, 58.68; H 9.55, 9.56.
$C_5H_{10}O_2$. Computed %: C 58.82; H 9.8.

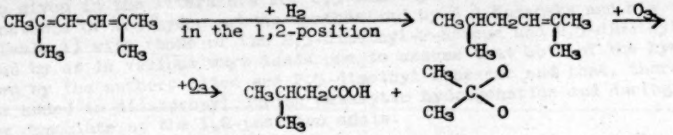
* The preparation of this composite contact agent has been described previously [2].

** In our first attempts to reduce diisocrotyl, we used only 7 g of sodium per 10 g of diene; the reduction of the diisocrotyl was incomplete, 65% of the initial diene being recovered unchanged.

The m.p. of the phenylphenacyl ester of this acid was 77°.

Literature data for isopropylacetic acid: Conrad and Bischoff [7] - b.p. 174° (765 mm); Schmidt and Sachtleben [8] - b.p. 175° (754 mm); Drake and Bronitsky [6] - m.p. of phenylphenacyl isopropylacetate is 76°.

The synthesis of acetone peroxide and isopropylacetic acid when the hydrocarbon is ozonated indicated that it was 2,5-dimethyl-2-hexene and, hence, that hydrogen was added to the diisocrotyl at the 1,2-position during reduction with sodium in liquid ammonia:



For the sake of comparison with the constants of the synthesized hydrocarbon, the data in the literature for two possible products of the partial reduction of diisocrotyl: 2,5-dimethyl-2-hexene (I) and 2,5-dimethyl-3-hexene (II), are listed in Table 1:

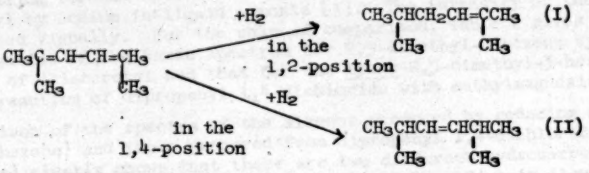


TABLE 1

	2,5-dimethylhexenes	B.p.	n_D^{20}	d_4^{20}	Author
1	Trans-2,5-dimethyl-3-hexene, by reaction of dipropenyl-1,4-dichloride with methylmagnesium bromide (II)	103-103.5° (756 mm)	1.4100	0.7122	R.Ya.Levina, V.R.Skvarchenko, and E.G.Treshchova [9]
2	2,5-Dimethyl-2-hexene, synthesized by the reduction of diisocrotyl by sodium in liquid ammonia (I)	111.2-111.5° (747 mm)	1.4120	0.7182	Synthesized in the present research.
3	2,5-Dimethyl-2-hexene *	112-112.2 (760mm) 111.3-111.5(744mm)	1.4146	0.7202	Hull, Boord [10]
4	2,5-Dimethyl-2-hexene *	112.3 (760 mm)	1.4144	0.7190	Rudel [11]
5	2,5-Dimethylhexene, synthesized by reducing diisobutenyl by calcium ammoniate	110-111 (759 mm)	1.4103	0.7169	B.A.Kazansky and N.F.Glushnev [12]
6	2,5-Dimethylhexene, synthesized by hydrogenating diisocrotyl in the presence of platinum black	110-112	1.4103 at 18°)	0.7136 (at 17°)	B.A.Kazansky and E.P.Mikheyev [13]

* The synthesis of 2,5-dimethyl-2-hexene has not been described in the literature; its constants are given in Egloff's handbook [14], which cites the dissertations by Hull and Boord [10] and Rudel [11].

The figures in Table 1 indicate that the 2,5-dimethyl-2-hexene (I) produced in our research by the partial reduction of diisocrotyl by sodium in liquid ammonia has a boiling point and a specific gravity that differ considerably from those of the 2,5-dimethyl-2-hexene (I) synthesized by us previously [9] by reacting CH_3MgBr with dipropenyl 1,4-dichloride. These constants agree almost perfectly, however, with those given in the literature for 2,5-dimethyl-2-hexene [10,11]. A comparison of the constants of the hydrocarbons synthesized by B.A.Kazansky and his co-workers [12,13] (Table 1) with those of the 2,5-dimethyl-2-hexene and 2,5-dimethyl-3-hexene synthesized by us in various ways leads one to assume that both of the hydrocarbons synthesized by the authors cited are 2,5-dimethyl-2-hexene and that, therefore, hydrogen was added to diisopropyl during catalytic hydrogenation and during reduction by calcium ammoniate at the 1,2-position again.

3. Optical Analysis of the 2,5-Dimethyl-2-Hexene Synthesized by the Partial Reduction of Diisopropyl

The Raman spectra of the 2,5-dimethyl-2-hexene were recorded under conditions like those prevailing for the spectra of the hydrocarbons resulting from the reduction of dipropenyl by sodium in liquid ammonia [1]. The intensity of the spectrum lines was evaluated visually. For the sake of comparison, Table 2 gives the frequencies and intensities of the Raman spectrum for 2,5-dimethyl-2-hexene synthesized by the reduction of diisocrotyl and that for the trans-2,5-dimethyl-3-hexene synthesized by the reaction of dipropenyl 1,4-dichloride with methylmagnesium bromide [9].

A comparison of the spectra of the alkenes produced by reducing diisocrotyl (2,5-dimethyl-2-hexene) and those prepared from dipropenyl 1,4-dichloride (2,5-dimethyl-3-hexene) clearly shows that these are two different hydrocarbons. The spectrum of the alkene synthesized by reducing diisocrotyl by sodium in liquid ammonia contains a number of lines of average intensity (324, 474, 1072, 1241, 1270, and 1330 cm^{-1}) that are lacking in the spectrum of the alkene prepared from dipropenyl 1,4-dichloride. On the other hand, the spectrum of the latter hydrocarbon contains several lines that are absent in the spectrum of the first hydrocarbon – 337, 460, 831, 1040, and 1300 cm^{-1}.

The frequency of 1674 cm^{-1} for the double bond in the spectrum of hydrocarbon (I), synthesized by the reduction of diisocrotyl, may denote either a trans form of an RCH=CHR(A) alkene or an alkene of one of the two following types: $RR'C{=}CR^2R^3$ (B) or $RR'C{=}CHR^2$ (C).

Consideration of these three possible cases enables us to arrive at the following conclusions: if the hydrogen were added to the diisocrotyl at the 1,4-position, the reaction product would have to be 2,5-dimethyl-3-hexene, i.e., a hydrocarbon of type A. But, as has already been pointed out above (Table 2 and the conclusions drawn therefrom), the spectrum of the synthesized alkene is quite different from the spectrum of trans-2,5-dimethyl-3-hexene, prepared from dipropenyl 1,4-dichloride [9].

The second possibility, a structure of the $RR'C{=}CR^2R^3$ (B) type, likewise had to be rejected, since it did not conform to the carbon skeleton of the initial diisocrotyl > C=CH–CH=C <.

The third possibility, a structure of the $RR'C{=}CHR^2$ (C) type, defined by the frequency 1674 cm^{-1}, agrees fully with a product of the reduction of diisocrotyl at the 1,2-position, i.e., with 2,5-dimethyl-2-hexene.

TABLE 2

Spectrum of 2,5-dimethyl-2-hexene (I)		Spectrum of 2,5-dimethyl-3-hexene (II)	
Frequency	Intensity (visual)	Frequency	Intensity (visual)
224 •	1	–	–
226 •	1; w	269 •	2
276 - 293 •	0.7; w	276 - 294 •	2
324	5	–	–
–	–	337	2
373	1	373	0.75
383 - 397	2; w	387 •	0.5
–	–	411	0.9
424-446	1, 2; w	434	1.5
–	–	460	3.5
–	–	467 •	0.5
474	3.5	–	–
503	1, 3; b	500	3; b
547	0.8	546	0.5
555	1.5	–	–
587	1; b	–	–
635 •	0.5	612 •	0
671 •	1	671 •	1
707	1; b	702	1; b
746	1	–	–
772	6; w	770	1.5; w
796-809	3; w; b	804	3.5
–	–	831	3
854	4.5	855	3.5
891	1.3	887	1
921	0.7	920	3.5
947	2	–	–
957	2.5	956	5
985	1.5; b	985	2; b
1015	0.7	–	–
–	–	1022 •	0
–	–	1040	2; w
1072	1.6	–	–
1086	1.1	–	–
1107-1117	3; w; b	1104	5; w
1144	0.2	–	–
1170	1.2	1170	2.2; w
1200	0.9	–	–
1241	2.2	–	–
–	–	1254	0.7; w
1270	2.8	–	–
–	–	1296 1302	10; w
1330	7	–	–
1354	1.25	–	–
1382	8	1382	2.5
1440-1460	10; w	1440-1460	10; w
1571	1	1571	1.4
–	–	1611	1.7
1620	1.2	–	–
1652 •	0.12	–	–

(continued on next page)

• See footnote on following page.

TABLE 2 (continued)

Spectrum of 2,5-dimethyl-2-hexene (I)		Spectrum of 2,5-dimethyl-3-hexene (II)	
Frequency	Intensity (visual)	Frequency	Intensity, (visual)
-	-	1668	20
1674	17	-	-
2877	4; b	2876	3.5; b
2930	3	-	-
-	-	2942	0.75
2967	1.6	2965	1.5
3051	0.4; b	3051	0.7; b
-	-	3128	0.5
3141	0.6	-	-

*The following notation is used to denote combined lines: w - wide band; b - background. Each spectrum was recorded twice, the frequency values being almost identical in both instances. Whenever they differed slightly, the mean value of two measurements was taken. The asterisks denote lines that were found in only one of the spectra.

SUMMARY

1. The partial reduction of diisocrotyl - a symmetrical alkadiene with conjugated double bonds - by sodium in liquid ammonia has been studied for the first time.

2. It has been established that when diisocrotyl is partially reduced by sodium in liquid ammonia, hydrogen is added at the 1,2-position, forming 2,5-dimethyl-2-hexene - a hydrocarbon that has no centrally located double bond (73% of the theoretical yield).

3. The structure of the synthesized hydrocarbon (2,5-dimethyl-2-hexene) has been proved by its constants, by analysis, by a study of its ozonation products, and by analysis of its Raman spectrum.

4. The results obtained in the present (and the previous) research refute the established notion that hydrogen is added to a system of conjugated double bonds "the instant it is formed" at the 1,4-position, independent of the structure of the hydrocarbon.

LITERATURE CITED

[1] R.Ya. Levina, V.R.Skvarchenko, V.M.Tatevsky, and E.G.Treshchova, J.Gen.Chem., 20, 684 (1950)*
[2] R.Ya.Levina, L.A.Derendyayeva, and A.A.Fainzilberg, J.Gen.Chem. 16, 817 (1946).
[3] Ch.Prevost, Comptes rendu., 184, 1460 (1927).
[4] A.Henne, H.Chanan, J.Am.Chem.Soc., 66, 395 (1944).
[5] A.Bayer, V.Villiger, Ber., 23, 124, 858 (1900).
[6] N.Brake, J.Bronitsky, J.Am.Chem.Soc., 60, 1717 (1938).
[7] Conrad, Bischoff, Lieb. Ann., 204, 151 (1880).
[8] E.Schmidt-Sachtleben, Lieb.Ann., 193, 92 (1880).
[9] R.Ya.Levina, V.R.Skvarchenko, and E.G.Treshchova, J.Gen.Chem. 20, 445 (1950).**
[10] C.Hull,C.Boord, Thesis, Ohio State U. Abs.Drs. Dissertations, N 18, 191 (1936).
[11] H.Rudel. Thesis Ohio State U., Sept. (1938).
[12] B.A.Kazansky, N.F.Glushnev, Izv.USSR Acad.Sci, Chem.Ser., 4, 1065 (1938).
[13] B.A.Kazansky, E.P.Mikheyev, Sci.Pap. Moscow State Univ., 199 (1941).
[14] G.Egloff, Physical Constants of Hydrocarbons, page 227.

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*See CB translation of previous article.
**See CB translation p. 469 ff.

SEGREGATED CHROMOPHORIC SYSTEMS

XXVI. COLOR PHENOMENA IN NITROPHENACYL DERIVATIVES OF THE AROMATIC AMINES

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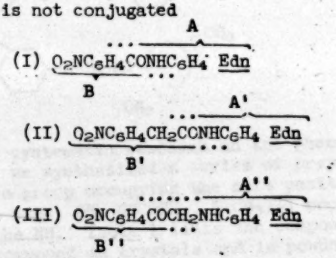
Like the aryl amides of nitrobenzoic (I) [1] and nitrophenylacetic (II) [2] acids previously synthesized by us, the nitrophenacyl derivatives (III) are also compounds with segregated chromophoric systems, i.e., compounds in which the electronophile nitro-enoid* system (B'') is not conjugated



with the donorenoid** system (A'') and which are built up according to the general formula (IV) Eph C_6H_4 Q C_6H_4 Edn, where Eph is an electronophile group*** (NO_2 in this instance), Edn is an electrodonor group (OCH_3, OH, $N(CH_3)_2$, etc.), and Q is a group that disturbs the conjugation of double bonds ($-COCH_2NH-$ in this instance).

Research on nitrophenacyl derivatives attracted us especially since, from the standpoint of the notions we have developed (according to which the most important factor governing the color of compounds with segregated chromophoric systems is the direct interaction between these systems due to exomolecular forces****), the phenomenon of color ought to be much more intense in nitrophenacyl derivatives than in the derivatives of nitrophenylacetic acid that are insoluble with them, and even more intense than in nitrobenzoyl derivatives.

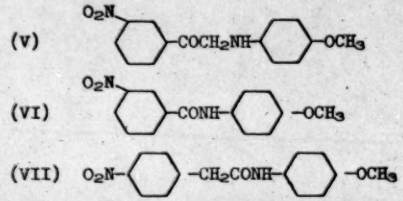
* Nitro-enoid system - a system of conjugated double bonds with a nitro group attached to it.

** Donorenoid system - a system of conjugated double bonds with an electrodonor group attached to it.

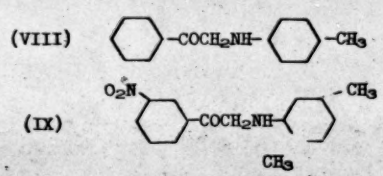
*** Cf the paper by V. A. Izmailsky [3] for the terms "electronophile" and "electronodonor".

**** Exomolecular forces are forces of the external field, which may bring about reactions between chromophoric systems or between individual molecules or within the molecule (the latter reaction occurring when the steric conditions are favorable) [4].

The data on the coloration of some of the nitrophenacyl derivatives we have found in the literature corroborated our hypotheses. Compound (V) is red, for example, whereas its corresponding nitrobenzoyl derivative (VI) is merely pale yellow,



and the derivative of nitrophenylacetic acid (VII) is colorless [2], notwithstanding the position of the NO_2 group in the last compound, which is more favorable for coloration. Compound (VIII) is yellow [8], whereas compound (IX) is brick-red [7], in spite of the fact that the methyl groups act as supplementary donor (auxochrome) groups in these compounds, and even the NO_2 group is missing in the first one of them.



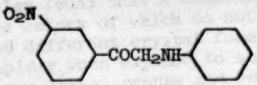
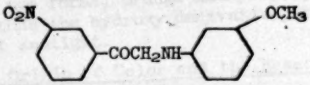
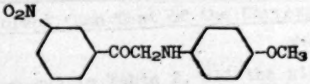
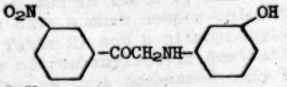
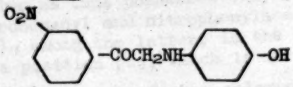
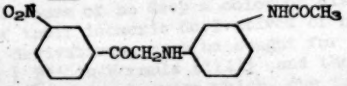
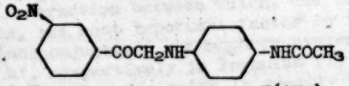
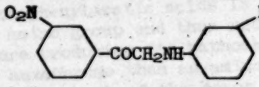
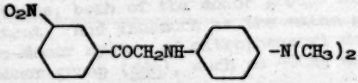
In order to carry out systematic research on the phenomenon of color in several nitrophenacyl derivatives, we synthesized a series of preparations, with the general formula of (III), the nitro group occupying the meta position with respect to the CO, and the donor group [Edn = OCH_3, OH, $NHCOCH_3$, $N(CH_3)_2$] occupying the para or meta position with respect to the NH. Table 1 lists the compounds we synthesized with a note on the color of the compound in crystals and in powder. Inasmuch as the melting points of most of the compounds listed vary with the rate of heating, these melting points are not listed in the table, but are given solely in the experimental section.

All the compounds we synthesized have an intense color. Even the simplest representative of this series of compounds [8], which has no supplementary donor group (Compound 1, Table 1), is an intense yellow. Introduction of an auxiliary donor group at either the para or the meta position with respect to NH deepens the color. When even the comparatively weak supplementary donor group, OCH_3, is present, the corresponding compounds prove to be either orange-colored* (m-OCH_3) or light-red (p-OCH_3) (Compounds 2 and 3, Table 1). Hydroxy derivatives are colored orange-red or red (Compounds 4 and 5, Table 1), while compounds with the most powerful donor group, $N(CH_3)_2$, are reddish-brown and brownish-red, respectively (Compounds 8 and 9, Table 1).

We have also included compounds with an $NHCOCH_3$ group as a second donor group in this series of nitrophenacyl derivatives. The color of these compounds is closest

*In the literature the color of these compounds is given as red [cf Formula (V) above].

TABLE 1

No.	Formula of compound	Color of substance in crystals	Color of substance in powder
(I)		Intense yellow	Yellow
(II)		Orange *	Yellow orange
(III)		Light-red	Reddish-orange
(IV)		Orange-red **	Red-orange
(V)		Red	Orange-red
(VI)		Reddish-orange	Yellow-orange
(VII)		Red-orange	Yellowish-orange
(VIII)		Red-brown ***	Red-brown
(IX)		Brown-red	Brown-red

to that of derivatives containing the OCH_3 group: compounds with an $NHCOCH_3$ group in the meta position are reddish-orange, and red-orange with the group in the para position (Compounds 6 and 7, Table 1). As has been stated above, the corresponding methoxy derivatives are colored orange and light red. Thus, in this instance the chromo-

* Another form of this compound is yellow.

** The substance exists in two forms, if identical in color, but with different melting points and crystallizing differently.

*** Another form of this compound is carmine-red.

phore properties of the acetoamino group most closely resemble those of the OCH_3 group.*

We also found that a compound with an OH group in the meta position exists in two forms, the colors of which do not differ perceptibly, but which have different melting points and different crystal forms. One of these forms is photosensitive, turning red fairly rapidly when exposed to sunlight. Compounds with an m-OCH_3 group are also produced in two forms, orange and yellow, the former likewise being photosensitive, even more so than the hydroxy derivative; the preparation turns red very quickly when exposed to direct sunlight.

The Origin of Color and the Reason for the Deeper Color of Nitrophenacyl Derivatives than That of the Corresponding Derivatives of Nitrobenzoic and Nitrophenylacetic Acids

As we see in Table 2, all the nitrophenacyl derivatives synthesized by us (No. 1, Table 2) have a much deeper color than the analogous derivatives of m-nitrobenzoic [1] (No. 2, Table 2) and p-nitrophenylacetic acids [2] (No. 3, Table 2) described previously. The nitrophenylacetic derivative with the weakest donor group, m-OCH_3, has the same color as that possessed only by compounds with the strongest donor groups among the nitrobenzoyl and nitrophenylacetic derivatives: m-$N(CH_3)_2$ in the former and p-$N(CH_3)_2$ among the latter; in the latter series of compounds the NO_2 group occupies the para position [1];** which is more favorable for color.

The cause of so deep a color of nitrophenacyl derivatives, which far exceeds the color of their isomeric derivatives of nitrophenylacetic acid or the color of nitrobenzoyl derivatives, must be sought for in the structural peculiarities of the electronophile [B'' in Formula (III)] and the donorenoid (A'' in that formula) systems, the direct interaction between which, due to exomolecular forces, is, according to our concepts, the most important factor in the color phenomena of compounds with segregated (nonconjugated) chromophore systems. Whereas the two-donor system NHC_6H_4 Edn [A and A', respectively in Formulas (I) and (II)] in the derivatives of nitrobenzoic and nitrophenylacetic acids is greatly weakened by the CO group, directly attached to the amino group and thus reducing the latter's donor properties considerably, and therefore producing its bathochrome effect (as we know, an acyl amino group is a much weaker auxochrome than an amino group), this weakening does not exist in nitrophenacyl derivatives, both of the donor groups exhibiting their bathochrome action to the fullest extent. And inasmuch as the amino group is one of the most powerful donor groups, the two-donor system of nitrophenacyl derivatives is strong enough when a weak auxiliary donor group (Edn), such as $-OCH_3$ or even $-CH_3$, is present.

On the other hand, the electronophile system of nitrophenacyl derivatives [B'' in formula (III)] is likewise much stronger than in the derivatives of nitrobenzoic and nitrophenylacetic acids [B and B' in Formulas (I) and (II)]. In the compounds of the latter two series, the electronophilia of the CO group is considerably weakened by the action of the adjoining NH group, (the CO in an amide group is neutralized, so to speak).*** This weakening action is not present in nitrophenacyl derivatives, all the chromophoric properties of the CO group being manifested. Hence, the presence of a CH_2 group between the CO and NH groups in these compounds is a factor that promotes color phenomena, for it results in deeper color, owing to a strengthening of the electronophile and donorenoid systems.

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* According to the theory of mesomerism, a donor group, (an auxochrome) may be considered to be a chromophore of a special type [3].

** No analogous derivatives of meta-nitrophenylacetic acid have been described.

*** Thus it exhibits only slight cromophoric properties.

TABLE 2

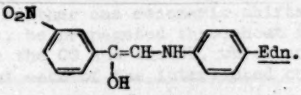
No.	Type of compound	Substituting donor group (Edn) and color of the respective compound as a powder					
		m-OCH_3	n-OCH_3	m-OH	n-OH	m-$N(CH_3)_2$	n-$N(CH_3)_2$
1	O_2N–C$_6$H$_4$–$COCH_2NH$–C$_6$H$_4$–Edn	Yellow-orange	Reddish-orange	Red-orange	Orange-red	Red-brown	Brownish-red
2	O_2N–C$_6$H$_4$–CONH–C$_6$H$_4$–Edn	Color-less	Light yellow	Pale yellow	Light yellow	Yellow-orange	Light red, brownish tint
3	O_2N–C$_6$H$_4$–CH_2CONH–C$_6$H$_4$–Edn	Color-less	Color-less	Pale yellow-ish	Nearly color-less	Orangish yellow	Yellow-orange

The Possibility of Tautomeric Rearrangement in Nitrophenacyl Derivatives

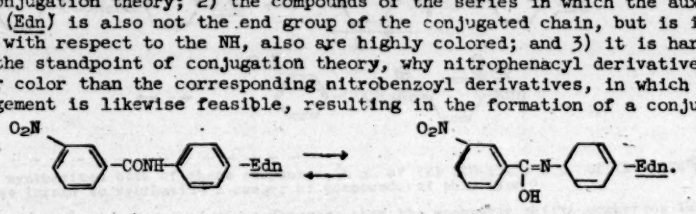
It should be borne in mind, however, that the hydrogen atoms in the CH_2 group, which are influenced by the negativing CO group, possess considerable mobility, which makes possible a tautomeric rearrangement to the $-COCH_2NH-$ group:

$$-COCH_2NH- \rightleftharpoons -C(OH)=CHNH-$$

Then, from the standpoint of the conjugation theory [10], the cause of color might be sought in the possible formation of a compact conjugated system, with another donor at one end, on the assumption that the NH group may serve as the conjugation guide, like the $-CH=CH$ [11]:

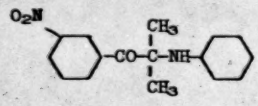


The following arguments may be brought forward, however, in refutation of this: 1) in all the compounds we have considered, the nitro group is in the meta position and hence is not the end group of a conjugated chain, which is essential according to the conjugation theory; 2) the compounds of the series in which the auxiliary donor group (Edn) is also not the end group of the conjugated chain, but is in the meta position with respect to the NH, also are highly colored; and 3) it is hard to explain, from the standpoint of conjugation theory, why nitrophenacyl derivatives have a much deeper color than the corresponding nitrobenzoyl derivatives, in which tautomeric rearrangement is likewise feasible, resulting in the formation of a conjugated chain:

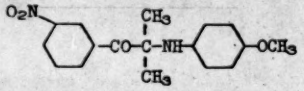


It is not likely that lengthening the conjugated chain by one link could result in so considerable deepening of the color; 4) it is still harder to explain, from the standpoint of conjugation theory, why the derivatives of p-nitrophenylacetic acid, in which the formation of a conjugated chain is also conceivable and which are as long as the chains of nitrophenacyl derivatives:

are much less deeply colored, in spite of the fact that in these compounds the nitro group is in the para position, which is much more favorable for color, and is the end group of the conjugated chain; and 5) perhaps the most convincing argument against the conjugation theory is the fact, established by us, that when the active hydrogen atoms are replaced by methyl groups in nitrophenacyl derivatives (making tautomerization and, hence, the formation of a conjugated chain wholly impossible), we get compounds that are also intensely colored; for example, compound (X) is intensely yellow in its crystalline state, while compound (XI) is orange-red.*



(X)

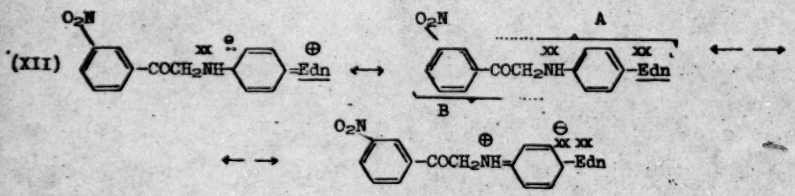


(XI)

6) Lastly, it must be remembered that the recent paper by V.A.Izmailsky and A.M. Simonov, in which the role of the NH group in diphenylamino derivatives is elucidated, casts doubt upon the very possibility that the NH group is a conjugation guide.

Hence, we cannot look to the possibility of tautomeric rearrangement as the fundamental cause of color in nitrophenacyl derivatives.

On the other hand, neither can mesomeric shifts of electrons, which may occur in this series of compounds, be propagated throughout the molecule (owing to the presence of the CH_2 group between the CO and the NH, which acts as an insulator); they must be confined to the limits of each of the interlinked conjugated systems [A and B in Diagram (XII)].**



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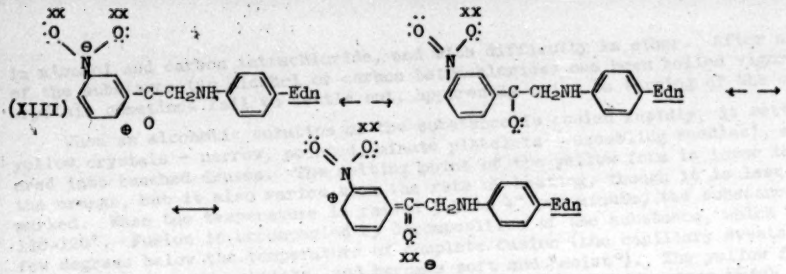
*We have synthesized both of these compounds [b p of (X) 120-121°; b p of (XI) 124°] In the near future we intend to synthesize a number of compounds of this type

**It must be borne in mind that these diagrams show the mesomeric shifts occurring in an electronophile nitro-enoid system (XIII) and in a donorenoid system (XII) separately, the shift to the ortho position being omitted. A full expression of the meso state of the molecule requires an allowance for the fact that these electron shifts may occur simultaneously in both systems.



That is why the molecule of a nitrophenacyl derivative must be considered to be a compound built up from two separate systems, which interact as the result of exomolecular forces (complex mesomerism [9]), rather than as a single mesomeric system with an overall conjugated chain. And it is to this interaction that we must look for the basic cause of the color of the compounds in question.

EXPERIMENTAL

The ω-bromo-3-nitroacetophenone needed for synthesizing the preparations of this series was prepared by nitrating acetophenone and then treating the nitro product with bromine [13].

N-[3-Nitrophenacyl]-p-anisidine (No. 3, Table 1). 2.46 g (0.02 mol) of p-anisidine and 2.3 g (0.01 mol) of ω-bromo-3-nitroacetophenone were dissolved in 20 ml of alcohol by heating to the boiling point. The crystalline deposit that settled out after the solution cooled was washed with alcohol and warm water and then recrystallized, first from alcohol and then from benzene. This yielded light-red crystals as long, narrow lamellae, whose melting point varied with the rate of heating: when the temperature rises 3.5-4° per minute, fusion takes place at 134-135°, accompanied by decomposition of the substance; if heating is speeded up, the melting point rises; if the heating is slower, on the other hand, the melting point is lower, with gradually increasing sweating of the capillary taking place a few degrees before melting sets in. [The melting point of this compound (139°) given in the literature is observed when the temperature rises 6 to 7° per minute.]

The synthesized compound is readily soluble in acetic acid and acetone, fairly soluble in benzene, less soluble in alcohol, and soluble with difficulty in ether and carbon tetrachloride.

0.1235 g substance: 10.71 ml N_2 (21°, 754 mm).
Found %: N 9.82.
$C_{15}H_{14}O_4N_2$. Computed %: N 9.79.

N-[3-Nitrophenacyl]-m-anisidine (Table 1, No. 2). This substance was synthesized by a procedure like that used above. Double recrystallization from alcohol yielded the product as orange lamellar crystals, whose melting point – as in the preceding preparation – varies with the rate of heating: when the temperature is raised 3.5 to 4° per minute, the substance fuses at 125-126° with decomposition; at a faster heating rate the melting point is higher, and with a slower heating rate, it is lower; the capillary is observed to start sweating a few degrees before fusion begins.

The substance is readily soluble in acetone, acetic acid, and benzene, less so

in alcohol and carbon tetrachloride, and with difficulty in ether. After a solution of the substance (in alcohol or carbon tetrachloride) has been boiled vigorously, the crystals sometimes fail to settle out, apparently owing to tarring of the substance.

When an alcoholic solution of the substance is cooled rapidly, it settles out in yellow crystals – narrow, pointed, minute platelets (resembling needles), mostly gathered into bunched druses. The melting point of the yellow form is lower than that of the orange, but it also varies with the rate of heating, though it is less sharply marked. When the temperature is raised 3.5 to 4° per minute, the substance fuses at 118-120°. Fusion is accompanied by decomposition of the substance, which begins a few degrees below the temperature of complete fusion (the capillary sweats, and the substance turns red, shrinks, and becomes soft and "moist"). The yellow form may also be produced by crystallization from carbon tetrachloride, from which solvent it is sometimes recovered even when the solution is chilled slowly. The orange form is photosensitive: the surface of the substance gradually turns red when exposed to light. This reddening takes place rapidly in direct sunlight, the surface of the substance turning a dark-red. Endeavors to recrystallize the red substance produced from the orange form by turning it into a fine powder and keeping it in direct sunlight for several days until all of it had reddened were unsuccessful; the substance was recovered in its yellow form from an alcoholic solution as well as from a solution in carbon tetrachloride. The yellow form is almost insensitive to light.

Orange form: 0.1566 g substance: 12.92 ml N_2 (17°, 766 mm).
Found %: N 9.71.
$C_{15}H_{14}O_4N_2$. Computed %: N 9.79.

Yellow form: 0.1574 g substance: 13.34 ml N_2 (18°, 764 mm).
Found %: N 9.84.
$C_{15}H_{14}O_4N_2$. Computed %: N 9.79.

N-[3-Nitrophenacyl]-p-aminophenol (Table 1, No. 5). 1.1 g (0.01 mol) of p-aminophenol and 2.3 g (0.1 mol) of ω-bromo-3-nitroacetophenone were separately dissolved by heating in alcohol (the first in 50 ml, the second in 20 ml). The aminophenol solution, which turned brown, was decolorized by adding a small quantity of sodium hydrosulfite to it, after which sodium bicarbonate was added (1.25 g), and the solution of ω-bromo-3-nitroacetophenone was poured in. The red crystalline precipitate that soon settled out was filtered out and washed with alcohol and then with warm water. Double recrystallization from alcohol yielded long acicular (filiform) red crystals, whose melting point, as in the preceding preparations, varies with the heating rate and is accompanied by decomposition of the substance, which sets in even before fusion. When the heating rate is 3.5-4° per minute, the substance fuses at 134-135°. The product is readily soluble in acetone (even in the cold) and in acetic acid, less so in alcohol, with difficulty in benzene and ether, and with even greater difficulty in carbon tetrachloride.

0.1384 g substance: 12.40 ml N_2 (13°, 734.5 mm).
Found %: N 10.21.
$C_{14}H_{12}O_4N_2$. Computed %: N 10.30.

N-[3-Nitrophenacyl]-m-aminophenol (Table 1, No. 4). 1.25 g of sodium bicarbonate was added to a heated solution of 2.3 g of ω-bromo-3-nitroacetophenone in 20 ml of alcohol, after which a heated solution of the m-aminophenol (1.1 g in 10 ml of alcohol) was added. The mixture was stirred vigorously for a few minutes and then set aside to crystallize . The precipitate was filtered out and washed, first with dilute alcohol and then with warm water. Crystallization from alcohol yielded orange-red crystals, minute three-sided prisms with a m.p. of 146-147° (when the temperature was raised 3.5

to 4° per minute). Fusion was accompanied by decomposition of the substance. The product is readily soluble (even in the cold) in acetone and acetic acid, less so in alcohol and chloroform, with some difficulty in benzene, and with even greater difficulty in ether and carbon tetrachloride. When recrystallized from alcohol, the substance was recovered (with gradual cooling of the solution) in another form, which was likewise orange-red, but crystallized as long platelets with pointed ends, having a m.p. of 157-158° with decomposition (at the same heating rate). Contrary to the first form, the second is harder to dissolve in alcohol and chloroform and is sensitive to light: in direct sunlight it rapidly reddens (but more slowly than the corresponding methoxy derivative). When the reddened substance is recrystallized from alcohol, benzene, or chloroform, it is again recovered in the orange form.

First form: 0.1626 g substance: 14.68 ml N_2 (18°, 756.5 mm).
Found %: N 10.38.
$C_{14}H_{12}O_4N_2$. Computed %: N 10.30.

Second form. 0.1612 g substance: 14.69 ml N_2 (20°, 758 mm).
Found %: N 10.41.
$C_{14}H_{12}O_4N_2$. Computed %: N 10.30.

N-[3-Nitrophenacyl]-p-aminoacetanilide (Table 1, No. 7). 1.25 g of sodium bicarbonate was added to a warm solution of the bromide (2.3 g in 100 ml of alcohol), placed in a three-necked flask fitted with a mechanical stirrer, and then a warm solution of p-aminoacetanilide (1.5 g in 20 ml of alcohol) was added. The mixture was heated for a few minutes over a water bath (50-55°), and then it was set aside to be stirred without further heating. The precipitate that settled was filtered out 1½ hours later and twice recrystallized from alcohol after having been washed with alcohol and warm water. This yielded crystals as narrow long red-orange platelets that felted together. The melting point varies with the heating rate and is accompanied by decomposition, the first signs of which (sweating of the capillary) appear some 10 to 15° below the melting point. The substance fuses at 149-151° when the temperature is raised 3.5-4° per minute. The product is readily soluble in alcohol, and soluble with difficulty in benzene, ether, and carbon tetrachloride.

0.1412 g substance: 17.12 ml N_2 (22°, 752.5 mm).
Found %: N 13.62.
$C_{16}H_{15}O_4N_3$. Computed %: N 13.42.

N-[3-Nitrophenacyl]-m-aminoacetanilide (Table 1, No. 6). This was synthesized like the preceding preparation. Double recrystallization from alcohol yielded prismatic reddish-orange crystals that fuse at 163-165° (at a heating rate of 3.5-4° per minute) with decomposition. The capillary begins to sweat 3 to 5° below the melting point. The substance is readily soluble in acetic acid, somewhat less so in acetone, with some difficulty in alcohol, and with great difficulty in benzene, carbon tetrachloride, and ether. The preparation crystallizes readily from 1:1 dilute acetic acid, but when it is dissolved in acetic acid, it sometimes tars, no crystals being recovered.

0.1375 g substance: 16.15 ml N_2 (18°, 751 mm).
Found %: N 13.39.
$C_{16}H_{15}O_4N_3$. Computed %: N 13.42.

N-[3-Nitrophenacyl]-p-aminodimethylaniline (Table 1, No. 9). 1.25 g of sodium bicarbonate was added to an alcoholic solution of the bromide (2.3 g in 100 ml of alcohol), and then a solution of p-aminodimethylaniline (1.36 g in 15 ml of alcohol) was gradually added with mechanical stirring. The reaction took place at room temperature. After the mixture had been stirred for 1½ hours, the precipitate was

filtered out, washed with alcohol and warm water, and then twice recrystallized from alcohol. This yielded brown-red dense crystals, in druses of fanciful form. The melting point was 144-145° with decomposition at a heating rate of 3.5-4° per minute. The substance sometimes tars during the first crystallization from alcohol, and no crystals separate out. The product is readily soluble in acetone, acetic acid, and benzene, fairly readily in alcohol and carbon tetrachloride, and with difficulty in ether. The substance separates out of carbon tetrachloride in a lighter form (carmine-red), constituting long acicular crystals gathered into druses. The melting point is the same as that of the darker form.

0.1139 g substance: 14.24 ml N_2 (19.5°, 749 mm).
Found %: N 14.13.
$C_{16}H_{17}O_3N_3$. Computed %: N 14.05.

N-[3-Nitrophenacyl]-m-aminodimethylaniline (Table 1, No. 8). This was synthesized in the same manner as the preceding preparation. The precipitate was recrystallized from a 2:1 mixture of benzene and petroleum ether and then from alcohol. This yielded red-brown crystals as narrow, pointed platelets, forming fan-shaped druses. The melting point varies with the heating rate and is accompanied by decomposition of the substance, which sets in even before fusion. The substance fuses at 116-117° when the temperature is raised at a rate of 3.5-4° per minute. The product is readily soluble in acetone, acetic acid, and benzene, fairly readily in alcohol and carbon tetrachloride, and with difficulty in ether. The substance easily resinifies when it is heated in solution to the boiling point, and the crystals are often recovered in an impure state, sometimes not separating out at all. During crystallization it is desirable to take some more solvent to prevent the solution from boiling.

0.1186 g substance: 15.03 ml N_2 (22°, 754.5 mm).
Found %: N 14.27.
$C_{16}H_{17}O_3N_3$. Computed %: N 14.05.

SUMMARY

1. Starting with the assumption that the introduction of the CH_2 group in nitrobenzoyl aryl amides (I) between the CO and the NH groups ought to increase the electronophile (B) and the electronodonor (A) systems and, hence, deepen the color, we synthesized a number of the derivatives of nitrophenacyl derivatives with the general formula (II), in which the NO_2 group is in the meta position with respect to the CO, and the Edn [OCH_3, OH, $N(CH_3)_2$, and $NHCOCH_3$] is in the meta or para position with respect to the NH.

A

(I) $O_2NC_6H_4CONHC_6H_4$ Edn

B

A'

(II) $O_2NC_6H_4COCH_2NHC_6H_4$ Edn

B'

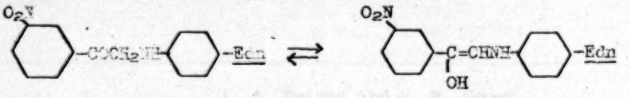
2. Our assumption was confirmed: all the compounds we synthesized had an intense color – from the orange (Edn = m-OCH_3) to brown-red [Edn = p-$N(CH_3)_2$] that was much deeper than the color of nitrobenzoyl derivatives or of the analogous derivatives of p-nitrophenylacetic acid.

3. The principal factor responsible for the phenomenon of color in nitrophenacyl derivatives is the direct interaction, due to exomolecular forces [4], between the electronophile nitro-enoid (B') and the donorenoid (A') systems.

4. The cause of the deeper color of nitrophenacyl derivatives, compared to that of the derivatives of p-nitrophenylacetic and m-nitrobenzoic acids, must be sought in

the structural peculiarities of nitro-enoid and donorenoid systems, which are considerably weakened in the last two series of compounds, as a result of the fact that the CO and NH groups, which are component parts of these systems, are linked together directly and therefore lose much of their inherent chromophoric properties. This weakening does not occur in nitrophenacyl derivatives.

5. It is not impossible that tautomeric rearrangements take place in nitrophenacyl derivatives, in accordance with Diagram (III), but this cannot be regarded as a fundamental factor responsible for the color of these compounds, inasmuch as the methyl

(III) 

derivatives (IV) $O_2NC_6H_4COC(CH_3)_2NHC_6H_5$ and (V) $O_2NC_6H_4(OC(CH_3)NHC_6H_4OCH_3$, in which such rearrangement is impossible, are also colored: (IV) is an intense yellow, and (V) an orange red.

6. The mesomeric shifts, which are possible in the molecule of a nitrophenacyl derivative owing to the presence of CH_2 (an insulator) between the CO and NH groups, cannot be propagated throughout the molecule and must be confined within the limits of each of the interconnected systems, the nitro-enoid and the donorenoid. Hence, the molecule of a nitrophenacyl derivative must be regarded, not as a single mesomeric system, but as a union of two segregated systems, which interact with each other as the result of exomolecular forces (complex mesomerism) [9].

LITERATURE CITED

[1] V.A.Izmailsky and E.A.Smirnov, J.Gen.Chem., 7, 513, 523 (1937); Bull.Soc. Chim., (5) 4, 81, 94 (1937); J.Gen.Chem. 8, 1730 (1938).

[2] V.A.Izmailsky and E.A.Smirnov, Dokl. USSR Acad.Sci., 20, 669 (1938).

[3] V.A.Izmailsky, J.Gen.Chem., 13, 685 (1943); also see: E.A.Smirnov, J.Gen. Chem., 17, 309 (1947).

[4] V.A.Izmailsky and P.A.Solodkov, Dokl. USSR Acad.Sci., 60, 587 (1948).

[5] M.Busch and F.Stratz, J.prak.Chem., 150, 30 (1937).

[6] E.Lellmann and A.Donner, Ber., 23, 187 (1890).

[7] F.Kunckell, Ber., 30, 573 (1897).

[8] R.Mohlau, Ber., 14, 171 (1881).

[9] V.A.Izmailsky. The Theory of the Color of Organic Compounds. Trans. 4th Conference on Problems of Aniline-Dye Chemistry, 13-15 October, 1939, USSR Acad.Sci. Press, 41-52 (1940).

[10] G.N.Lewis and M.Calvin, Chem.Rev., 25, 273 (1939); trans. in Prog.Chem., 10, 43, (1941); Th. Forster, Z. Elektroch., 45, 548, (1939); trans. Prog.Chem., 9, 100 (1940).

[11] W.Konig, J.prak.Chem., 112, 14 (1926).

[12] V.A.Izmailsky and A.M.Simonov, J.Gen.Chem. 16, 1659 (1946).

[13] H.Kortien, R.Scholl, Ber., 34, 1909 (1901).

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RESEARCH ON THE CHEMISTRY OF ALKENYNE SYSTEMS

I. THE ADDITION OF BROMINE TO VINYLACETYLENE

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In several reports published in this journal, one of the present authors described some new principles governing the addition reactions of various substances to divinyl and its homologs and halogen derivatives [1]. The discovery of these principles necessitated fundamental corrections of the electronic theory of the structure and reactions of compounds with conjugated double bonds [2]. In a series of reports, which we intend to publish in the near future, we shall discuss the patterns of behavior in the addition reactions of alkenyne compounds, particularly vinylacetylene.

During the 18 years that have elapsed since the discovery of vinylacetylene, the chemistry of this substance has been the subject of thorough research. Studies have been made of the numerous reactions involving the acetylenic hydrogen [3], the addition reactions at the multiple bonds [4-10], polymerization [11] and to some extent dimerization [12] reactions, and diene syntheses [13]. This paper is solely concerned with addition reactions.

The procedure involved in the addition of various substances to vinylacetylene has been reliably established in many cases. Hydrogen is chiefly added at the acetylenic bond, giving rise to divinyl, together with the products of further hydrogenation: butylenes and butane. Best results are obtained with electrolytic reduction [4]. When no catalysts are present, the hydrohalides are added at the ends of the conjugated systems, the hydrogen entering the first position. In the presence of catalysts, such as Cu_2Hal_2, addition takes place at the 1,2-position. These catalysts also promote the isomerization of 1,4-products to 1,2-products.

The α-chloro ethers are added only when catalysts are present, and then chiefly at the 1,4-position. But the products of 1,2-addition are formed at the same time, however. The same catalysts that promote addition also promote the isomerization of 1,4-products to 1,2-products [8]. Hence, in the last two cases it is not impossible for the 1,2-products to be formed, not as the result of an addition reaction, but by the isomerization of the 1,4-products initially formed.

Water [7] and organic acids [7] are added only when catalysts are present, and then only at the 1,2-position. The same 1,2-addition has been found to apply to methyl hypochlorite [9]. In the presence of alcoholates alcohols are added at the 1,4-position. There is some doubt regarding the manner in which alcohols are added in the presence of

boron fluoride [12].

The cited experimental data on the manner in which various substances are added to vinylacetylene conform with the singularities of the electron configuration of this substance [14]:

$$\overset{\curvearrowleft}{CH}\equiv C-\overset{\curvearrowright}{CH}=CH_2.$$

To begin with, the vinylacetylene molecule is more highly polar than divinyl, the first carbon atom being most highly negative and hence the point initially attacked in addition reactions. In fact, the manner in which such substances as hydrohalides and α-halogen ethers are added to vinyl acetylene bears out this conclusion.

On the other hand, in the vinylacetylene molecule the 1,4-position ought to be more active than in divinyl, and this, in turn, ought to promote addition principally at this position. The experimental data corroborate this conclusion as well: if no isomerization catalysts are present, addition usually takes place at the 1,4-position. Especially characteristic is the 1,4-addition of hydrohalides and alcohols.

Notwithstanding the considerable interest displayed in research on the chemistry of vinylacetylene, far from all of even the simplest reactions of this substance have been adequately explored at the present time. For instance, no research has been done on the problem of the manner in which halogens are added to vinylacetylene. And this problem is of considerable interest, both as regards the theory of the reactions of conjugated systems and for the expansion of the possibilities of organic syntheses based on vinylacetylene.

Only two papers deal with the reaction of vinylacetylene with the halogens, one of them being merely a preliminary report. A study has been made of the photochemical and thermal reactions of vinylacetylene with chlorine and bromine [15]. Chlorination of vinylacetylene in the gas phase yielded two dichlorides, a tetrachloride, and a hexachloride. Their structure was not established. Bromination of vinylacetylene yielded nothing but the tetrabromide. Nor was the structure of this substance established.

In a preliminary report on the halogenation of vinylacetylene, one of the present authors demonstrated that when vinylacetylene is chlorinated (100% excess) in chloroform at -10°, considerable hydrogen chloride is evolved, and large quantities of polymeric substances are formed. The dichloride output totaled only 15%. The ability of the dichloride mixture to polymerize was demonstrated by the presence of the dichloride – $CHCl=CCl-CH=CH_2$, the existence of a reaction involving the triple bond testifying to the presence of the isomeric dichloride – $CH\equiv C-CHCl-CH_2Cl$.

When the bromination of vinylacetylene under the same conditions was investigated, it was found that 1,2-dibromobutadiene-1,3 was formed, together with a dibromide with a b.p. of 70-76° at 10 mm, the structure of which was not completely established. All the dibromide fractions exhibited a triple-bond reaction, which indicates that an isomer with a triple bond, ($CH\equiv C-CHBr-CH_2Br$) was present [16].

The present report is devoted to a more detailed study of the bromination products of vinylacetylene. When bromine is added to vinylacetylene, the following three dibromides may be expected to result:

$CHBr=C=CH-CH_2Br$ (1); $CHBr=CBr-CH=CH_2$ (2); $CH\equiv C-CHBr-CH_2Br$ (3).

Most likely was the formation of the first two substances, inasmuch as position 1 ought to be the most active one in the vinylacetylene molecule. Of these two most likely addition products, the second ought to be more stable thermodynamically, inasmuch as its

molecule retains the conjugated double bonds. On the other hand, the 1,4-product ought to be considered more probable from the kinetic standpoint, inasmuch as the 1,4-position is especially active in the vinylacetylene molecule.

Examination of the electron configuration of the 1,4-product indicated the possibility of its isomerizing in two ways: either with a shift of the allylic bromide from position 4 to position 2, or with a shift of hydrogen from position 4 to position 2, this isomerization being feasible under the conditions of the addition reaction as well.

$$CHBr{=}C{=}CH{-}CH_2{-}Br \longrightarrow CHBr{=}CBr{-}CH{=}CH_2$$

$$CHBr{=}C{=}CH{-}CHBr{-}H \longrightarrow CHBr{=}CH{-}CH{=}CHBr$$

Both of these isomerizations yield up energy as the result of the formation of systems of conjugated double bonds. The first type of isomerization was observed in the similarly constructed monobromide - $CH_2{=}C{=}CH{-}CH_2Br$ [5], and the second in the monobromide - $CHBr{=}C{=}C(CH_3)_2$ [17].

Likewise, we had to reckon with the possibility of the acetylenic dibromide isomerizing, giving rise to the allene 1,4-dibromide:

$$CH{\equiv}C{-}\underset{\displaystyle Br}{CH}{-}CH_2Br \longrightarrow CHBr{=}C{=}CH{-}CH_2Br.$$

Hence, we had to resolve the problem, not only of the end products of the bromination of vinylacetylene, but also of the possible initial products, if these products indicated a tendency to isomerize during the addition reaction.

Resolving the structure of the reaction products ought to have been facilitated by the following chemical peculiarities of the three possible dibromides: in the dibromide with Formula (1), the presence of an active bromine atom and the ability to form bromoacetic acid upon oxidation; in the dibromide with Formula (2), the presence of conjugated double bonds and the low activity of the bromine atom (both bromine atoms are attached to the double bond); and in the isomeric dibromide with Formula (3), the presence of an acetylenic grouping. Of all these three dibromides, only the 1,2-dibromobutadiene-1,3 has been described previously [18].

We brominated vinylacetylene in chloroform at -10°. Vacuum fractionation of the reaction products yielded two dibromide fractions and a mixture of tetrabromides, which were not analyzed further. The fraction with a 43-46° b.p. at 10 mm (60% by weight of the dibromides) was a yellow oil with a typical nonacrid odor and the following chemical properties:

1. When oxidized with permanganate, it yielded principally oxalic and carbonic acids, more than 85% of the bromine turning into an ionic state.

2. It reacted with alcoholic ammoniacal silver nitrate partially, forming a mixture of the acetylenide C_4H_2BrAg and silver bromide.

3. When treated with an alcoholic solution of KOH in the cold, the fraction lost 9.5% of the bromine at once, the rest of the reaction occurring very slowly. Diacetylene was found in the reaction mixture. The dibromide recovered from the mixture, which resisted the action of alkali, did not exhibit a triple-bond reaction; its properties very closely resembled those of the 1,2-dibromobutadiene-1,3 previously prepared by dehalogenating the bromoprene dibromide. When this dibromide was heated some more with an alcoholic alkali, the bromine atoms were gradually replaced by ethoxy groups, and some diacetylene was formed.

4. The fraction polymerized upon standing, forming a yellow, tarry, high-polymer product. Polymerization was accelerated by heating, or keeping in an open vessel; pyrogallol and hydroquinone retarded polymerization.

5. The substance was unchanged by heating with hydrobromic acid in ether solution.

All these facts led us to conclude that the fraction with a b.p. of 43-46° at 10 mm consists of a mixture of two dibromides - diene and acetylenic - with the former largely predominating.

The quantitative proportions of these two isomeric dibromides was determined by the behavior of the fraction toward alcoholic ammoniacal silver nitrate. The output of the acetylenide (C_4H_2BrAg + AgBr) was 11%. Hence, the fraction was a mixture of approximately 90% of the diene and 10% of the acetylene dibromides. The data on the action of alcoholic alkali in the cold upon this fraction agree with this figure. After the fraction had been treated with alcoholic alkali in the cold, 85% of the dibromide remained unchanged, not exhibiting a triple-bond reaction. Hence, the total acetylenic dibromide cannot exceed 15%.

9.5% of the bromine enters solution, as stated above. Hence, the acetylenic dibromide ought to total 9.5%, if both of the bromine atoms are detached simultaneously, and 19% if one one bromine atom is detached in the cold. Inasmuch as the reaction mixture exhibits the qualitative reactions for diacetylene, we may conclude that two atoms of bromine are detached (owing to the presence of a large excess of alkali), at least partially, and, hence, the acetylenic dibromide must be less than 19% in any event.

The dibromide with a b.p. of 70-72° at 10 mm (40% by weight of the dibromides) was a nearly colorless liquid with a sharp, lachrymatory odor; it manifested a tendency toward oxidation by atmospheric oxygen, with tarring. When this dibromide was oxidized with permanganate, a high yield of monobromoacetic acid was recovered, which led us to assign it an allene structure (1).

Of the chemical peculiarities of the allenic dibromide, the greatest interest is attached to the reactions of polymerization, isomerization, and dehalogenation. When allowed to stand for a long time in a closed vessel with pyrogallol, the allenic dibromide polymerizes faster than does the diene, but its polymerization sets in with some delay. When heated for 1 hour to 100° in an open vessel, more than 60% of the substance polymerizes, a polymer of fairly low molecular weight being formed. The as yet unpolymerized portion contains a certain amount of isomerization products. About 25% of the substance polymerizes when heated for 1 hour to 100° in a closed vessel with no stabilizers present. When heated for 4 hours with an ethereal solution of hydrobromic acid, the substance underwent no noticeable change. When heated under the same conditions with Cu_2Br_2, the allene dibromide is isomerized to 1,2-dibromobutadiene-1,3, a small amount of the acetylenic dibromide also being formed. Thus, the isomerization of the 1,4-dibromide involves a shift of the halogen rather than of the hydrogen.

When we compare these data with those on the isomerization of 4-bromobutadiene--1,2 and 1-bromo-3-methylbutadiene-1,2, we may conclude that if it is possible for an allene-1,3-diene isomerization to take place in this case with a halogen or hydrogen shift, only the former shift occurs.

The electron theory specifies both the possibility and the direction of the isomerization of the 1,4-product. Inasmuch as the bromine atom is more active in position 4, whereas the activity of the halogen is limited at the double bond, the main course of isomerization must be the allene-1,3-diene rearrangement in this instance.

The allene-acetylene rearrangement must play a minor role.

$$Br - CH = C = CH - CH_2Br \longrightarrow CH \equiv C - CHBr - CH_2Br$$

This is what happened in our experiment.

The allene dibromide readily evolves hydrogen bromide, forming 1-bromobuten-3-yne-1.

The assumed structure of the bromovinylacetylene is borne out by all of its physical and chemical properties.

The substance has the corrosive, insistent odor that is typical of acetylenic halogen derivatives. Its boiling point, specific gravity, and refractive index are very close to those of the 1-bromobuten-3-yene-1 synthesized by the action of hypobromite upon vinylacetylene. It resinifies with extraordinary ease. When reacted with an alcoholic alkali, even in the cold, it evolves bromine, turning into vinylacetylene. This property is an especially cogent proof of the structure assigned to the substance, inasmuch as the two other possible isomers ($CH\equiv C-CBr=CH_2$ and $CH\equiv C-CH=CHBr$) yield diacetylene when reacted with an alcoholic alkali.

The reaction of bromovinylacetylene with ammoniacal silver nitrate is a complex one, leading to the formation of silver vinylacetylenide (low yield), probably as follows:

$$CBr\equiv C-CH=CH_2 + Ag(NH_3)_2OH \longrightarrow CAg\equiv C-CH=CH_2 + NH_4OBr + NH_3.$$

The silver vinylacetylenide is thrown down as a precipitate; as the bromine, it remains in solution. Silver bromide is precipitated only when the solution is strongly acidified.

The activity of the bromine atom in the molecule of the allene dibromide is quite understandable, since it is allylic in its nature. What is specific in this case is the fact that this mobility of the bromine is combined with a high activity of the hydrogen at position 1. The latter is activated, first by the double bond, and second by the bromine atom.

It is interesting to compare the data on the reaction between vinylacetylene 1,4-dibromide and an alcoholic alkali with the data on the reaction of the same reagent with divinyl, chloroprene, and bromoprene 1,4-dihalides. Whereas the divinyl dichloride and dibromide yield diethers of erythrene glycol (only the halogen is replaced) when acted upon by an alcoholic alkali, the corresponding 1,4-dihalides of chloroprene and bromoprene also yield 1,2-dihalogen derivatives of butadiene-1,3 (hydrohalides being detached) with a yield going as high as 70% [19].

The course of the reaction depends here, too, upon the mobility of the hydrogen atoms. In the chloroprene and bromoprene 1,4-dihalides, the mobility of the hydrogen atoms is increased, evidently, by the effect of the halogens [21]

$$H - CHHal - C = CH - CH_2Hal$$
$$\downarrow$$
$$Hal$$

Thus, this investigation has established the fact that vinylacetylene yields all three possible dibromides when it is brominated: 1,2-dibromobutadiene-1,3 (55%); 1,4-dibromobutadiene-1,2 (40%); and 3,4-dibromobutyne-1 (about 5%).

These figures indicate that this reaction results in the formation of a considerable quantity of the thermodynamically less advantageous 1,4-dibromide, which can be

isomerized to a 1,2-product by the use of catalysts. The reason for the formation of a 1,4-product is the increased activity of the 1,4-position in the vinylacetylene molecule mentioned above.

Inasmuch as the end products of the addition of bromine to vinylacetylene display no noticeable tendency toward isomerization under the bromination conditions employed (low temperatures and the influence of hydrogen bromide) or during vacuum distillation, which was determined by means of special tests, it may be said that these end products are also the initial products of the bromination. The only possibility remaining is that isomerization takes place in the intermediate reaction complex, viz.: it is possible that addition takes place entirely at the 1,4-position but that within the reaction complex part of the 1,4-product manages to isomerize to 1,2- and 3,4-products. It is, of course, impossible to ascertain the existence of such isomerization by the methods of organic chemistry.

EXPERIMENTAL

A solution of 160 g of bromine in 150 ml of chloroform was added drop by drop at a temperature of -8 to -12°, with constant stirring, to a solution of 104 g of vinylacetylene in 500 ml of chloroform. Practically no hydrogen bromide was evolved. After the reaction was over, the excess vinylacetylene and chloroform were driven off at standard pressure or in vacuum over a water bath, but when the latter method was employed, the bath temperature was not allowed to exceed 40°. This change in the distillation conditions did not affect the composition of the reaction mixture. The aggregate output of the reaction products totaled 190 g, or 90% of the theoretical. When the reaction products were distilled in vacuum at 10 mm, the following fractions were recovered in one of the experiments (as the result of three distillations):

No.	B.p. at 10 mm	Weight (g)	d_4^{20}	n_D^{20}	MR_D	
					Found	Computed
1	43-46°	76.0	1.9640	1.5792	35.87	35.27
2	46-55	3.2				
3	55-69	2.0				
4	70-72	44.0	1.9884	1.6000	36.46	35.27
5	72-120	8.2				
6	116-117 (6 mm)	42.5	2.5293	1.6277	52.14	51.27
7	Residue	15.6				

Determination of the bromine in Fractions 1, 4, and 6 indicated that the first two are vinylacetylene dibromides, while the latter consists of tetrabromides. The results of analysis were as follows:

Fraction	Weight (g)	AgBr recovered (g)	Found % Br	Hypothetical formula	Computed % Br
1	0.1775	0.3151	75.54	$C_4H_4Br_2$	75.48
3	0.1850	0.3264	75.08	$C_4H_4Br_2$	75.48
6	0.1597	0.3247	86.52	$C_4H_4Br_4$	85.99

1. Analysis of the fraction with a b.p. of 43-46° at 10 mm. To explore the properties and determine the structure of the dibromides in the fraction, we examined its behavior when heated and when reacted with permanganate, alcoholic ammoniacal silver nitrate, and an alcoholic solution of a caustic alkali.

a) The constants of the substance remained unchanged after 10.6 g of the substance had been heated in an ethereal solution over a water bath for 4 hours with 10 ml of 25% hydrobromic acid. Nor did the amount of acetylenic dibromide, determined as specified in experiment "c" change. When the substance was heated under the same conditions for 4 hours, but with 2 g of Cu_2Br_2 present, the triple-bond reaction did not vanish. When 2.1 g of the substance in a 50% toluene solution (3 ml of toluene) was heated to 100° in a sealed ampoule for 1 hour, 20% of the substance polymerized.

b) The oxidation of 16 g of the fraction in aqueous-acetone solution required 61.6 g of potassium permanganate, which corresponds to 7.9 atoms of oxygen per molecule of the dibromide. After the manganese dioxide had been filtered out of the solution, the acetone had been driven off in vacuum, and the solution acidified with a 50% solution of H_2SO_4 (acidification was accompanied by the evolution of considerable CO_2), a total of 1.8 g of acids was extracted from the solution with ether. 10.3 g of bromine ion, or 85.3% of the bromine present in the initial dibromide, was found in the solution.

The acids recovered from the solution crystallized in part. The crystalline substance (0.6 g) was washed with ether and recrystallized from water, after which it fused at 100° and proved to be oxalic acid (mixed fusion test sample). The residue, 0.9 g of a brown oil, contained 56.7% of bromine and was not analyzed any further. It was probably bromoacetic acid with traces of other oxidation products (the computed percentage of bromine in bromoacetic acid is 57.5%). Thus, the substance oxidized to form carbonic and oxalic acids almost exclusively.

c) Treatment of 5.2 g of the fraction with an aqueous-alcoholic solution of ammoniacal silver nitrate, prepared with 8.5 g of $AgNO_3$, yielded 1.15 g of a crystalline deposit. Analysis (calcination) indicated that the substance is a mixture of the acetylenide C_4H_2BrAg and silver bromide. Hence, a complex base acts like an alcoholic solution of KOH, detaching hydrogen bromide from the acetylenic dibromide:

0.1958 g substance: 0.1739 g AgBr.

Found %: Ag 51.02.

$C_4H_2Br_2Ag_2$. Computed %: Ag 50.69.

According to the amount of the acetylenide precipitated, the fraction contained about 11% of the acetylenic dibromide. The residue recovered from the solution by dilution – a dibromide that did not react with reagents for an acetylenic bond – had a b.p. of 43.0° at 10 mm, d_4^{20} 1.9536.

d) 21.2 g of the fraction was added in the cold to a 20% alcoholic solution of 17 g of KOH. One hour later, the mixture was diluted with three times its volume of water, and the oil that separated out was removed from the solution (8.8 g, or 85% of the dibromide used). The solution was found to contain 2.26 g of bromine ion, which corresponds to the evolution of 9.5% of the bromine present in the initial amount of dibromide. The solution exhibited a positive reaction for diacetylene with the Strizhevsky and Chekhover reagent [22], as well as the yellow precipitate with ammoniacal silver nitrate and the red precipitate with Ilosvay's reagent that are characteristic of diacetylene. The unreacted dibromide had the following constants:

B.p. 43.0° at 10 mm; d_4^{20} 1.9536; n_D^{20} 1.5802; MR_D 36.10.

$C_4H_4Br_2$. Computed: MR_D 35.27.

The constants of 1,2-dibromobutadinen-1,3 were previously [18] found to be: b.p. 46° at 10 mm; d_4^{20} 1.9481; n_D^{20} 1.5792.

0.1402 g substance: 0.2479 g AgBr.
Found %: Br 75.24.
$C_4H_4Br_2$. Computed %: Br 75.43.

It did not exhibit the reaction for an acetylenic bond. When a sample of the substance was allowed to stand for 1 hour with a fourfold excess of a 20% alcoholic solution of KOH, a total of 2% of bromine was lost.

e) When 21.2 g of the fraction was heated for 1 hour over a water bath with a 20% alcoholic solution of 17 g of KOH, 11.1 g (46.6%) of the bromine entered solution. The oil recovered when the reaction mixture was diluted weighed 6 g; it was divided into the following two fractions by vacuum fractionation: 44-50° at 10 mm; and 1.4 g of residue. The fraction with a b.p. of 44-50° at 10 mm was found to have d_4^{20} 1.7921.

0.1903 g substance: 0.3102 g AgBr.
0.2339 g substance: 0.0917 g AgI (Zeisel).
Found %: Br 69.41; OC_2H_5 7.70.
$C_4H_4Br_2$. Computed %: Br 75.43.

The analysis data indicate that this fraction is a mixture of the dibromide with a product in which the bromine has been replaced by an ethoxy group. The extent of conversion is of the order of 8-12%.

The residue was a product of the further substitution of ethoxyl for bromine; it contains an even higher percent of ethoxy groups and a lower percentage of bromine.

0.1090 g substance: 0.0883 g AgBr.
0.2514 g substance: 0.4257 g AgI.
Found %: Br 34.47; OC_2H_5 32.50.
$C_4H_4Br(OC_2H_5)$. Computed %: Br 45.14; OC_2H_5 25.45.

The results of analysis enable us to conclude that the extent of conversion is of the order of 51-55%.

When the fraction was heated with an alcoholic base, gas was seen to evolve; it was absorbed in alcohol. Analysis of this gas showed that it was diacetylene, as was the case in Experiment "d".

2. Analysis of the fraction with a b.p. of 70-72° at 10 mm. To explore the properties and determine the structure of the dibromides in this fraction, we examined its reaction with permanganate, its behavior when heated with isomerization catalysts, and its reaction with alcoholic KOH.

a) 150 ml of acetone, 75 ml of water, and 20 g of H_2SO_4 were added to 10 g of the fraction, after which pulverized permanganate (20 g, a 25% excess) was added to the mixture in small batches, with constant stirring and chilling (the temperature was kept below 15°). After the reaction was over, the deposit of manganese dioxide was filtered out and washed on the filter with hot water, after which the filtrate was neutralized with $NaHCO_3$ and then distilled. The ether was driven off at ordinary pressure over a water bath, and most of the water was driven off in vacuum, the temperature of the vapor not being allowed to exceed 35°. As soon as crystallization set in, distillation was stopped. The acids were recovered from the mixture of salts by reacting the mixture with a 100% excess of 50% H_2SO_4 and then extracting it repeatedly with ether. After the ether extract had been desiccated, the ether was driven off on a water bath, and the residue was distilled in vacuum. The distillate crystallized. The crystals, pressed out between layers of filter paper and washed with petroleum ether, fused at 45°. Analysis indicated that this was bromoacetic acid.

0.0848 g substance: 0.1140 g AgBr.
Found %: Br 57.21.
$C_2H_3O_2Br$. Computed %: Br 57.51.

When the mother liquor was analyzed to determine its bromine content, the figure found (56.30% Br) was close to that of pure bromoacetic acid, which indicates that only traces of impurities were present. The output of bromoacetic acid was about 3 g (46% of the theoretical).

The formation of bromoacetic acid testified to the fact that the oxidizable bromide has a $CH_2Br-CH=$ group of atoms, i.e., that it is 1,4-dibromobutadiene-1,2.

b) 3 g of the dibromide was heated in an open test tube for 1 hour over a boiling water bath (with pyrogallol). This caused 60% of the substance to polymerize. The part that did not polymerize was distilled at 45-75° and 10 mm and, to judge by its refractive index (n_D^{20} 1.5972), it contained about 14% of the isomerization product: 1,2-dibromobutadiene-1,3.

When 2.1 g of the dibromide was heated with a 50% solution of toluene for 1 hour at 100° in a sealed ampoule, 25% of the substance polymerized. A solution of 3 g of the substance in 30 ml of ether was heated over a water bath for 4 hours with 10 ml of 25% hydrobromic acid. Its constants did not change.

c) A solution of 10.6 g of the dibromide in 50 ml of ether was heated for 4 hours over a water bath with 20 ml of 25% hydrobromic acid and 2 g of Cu_2Br_2. This resulted in a mixture of diene and acetylenic dibromides with a b.p. of 43-44° at 10 mm; d_4^{20} 1.9579 and n_D^{20} 1.5806.

The percentage of the acetylenic dibromide in this mixture was determined in the same way as for the first fraction of the vinylacetylene bromination products. It was found to be 4.7%. Thus, it has been established that copper bromide easily polymerizes the 1,4-dibromide to 1,2-dibromobutadiene-1,3 and an acetylenic dibromide.

d) To ascertain the behavior of the dibromide toward an alcoholic base, the following experiment was set up. A 20% solution of 6 g of KOH in ethyl alcohol was carefully added to a solution of 21.2 g of the dibromide in ethyl alcohol (+ hydroquinone). The precipitate of KBr that was thrown down at once weighed 10.3 g, which corresponds to a conversion of the order of 86%.

After the mixture had been heated over a water bath with a reflux condenser for 5 minutes (longer heating results in formation of a polymer and diminishes the output of the monobromide), it was diluted with water, and the reaction product was distilled with steam. The residue exhibited a neutral reaction and contained 1.4 g of bromine. Thus, conversion totaled 98.3%.

The oil that collected in the receiver was separated, washed with water, and desiccated over $CaCl_2$. The output totaled 7.9 g, or 60% of the theoretical. To judge from the constants and the analysis data, the substance was 1-bromo-buten-3-yne-1. The constants of the substance were:

B.p. 52-53° at 217 mm; d_4^{20} 1.4767; n_D^{20} 1.5136.
Literature data: b.p. 52-53° at 217 mm; d_4^{20} 1.4804; n_D^{20} 1.5187.

0.1505 g substance: 0.2167 g AgBr.
Found %: Br 61.27.
C_4H_3Br. Computed %: Br 61.01.

When reacted with an alcoholic alkali, the acetylenic bromide detaches bromine readily, forming vinylacetylene. When allowed to stand with a 100% excess of 25%

alcoholic KOH at room temperature, a weighed batch of the bromide lost 22% of its bromine during 5 hours as a bromine ion. When heated, bromine was evolved very rapidly. The vinylacetylene formed as the result of this reaction was driven off in alcohol and determined as white silver and yellow copper derivatives. When the bromide is reacted with alcoholic ammoniacal silver nitrate, a copious precipitate first settles out; it redissolves rapidly and all that remains are the lustrous, highly explosive crystals of silver vinylacetylenide. About 0.15 g of the acetylenide was recovered from 0.52 g of the dibromide when it was reacted with a reagent prepared from 1.6 g of $AgNO_3$. Yield: 38%. The substance was analyzed without purification.

0.1065 g substance: 0.0680 g AgCl.
Found %: Ag 63.85.
C_4H_3Ag. Computed %: Ag 67.87.

Silver bromide precipitated out of the solution only when the latter was heated with concentrated nitric acid.

SUMMARY

1. A study has been made of the reaction of vinylacetylene with bromine in a chloroform solution.

2. It has been proved that this reaction results in formation of all the three possible dibromides: 1,2-dibromobutadiene-1,3 (55%); 1,4-dibromobutadiene-1,2 (40%); and 3,4-dibromobutyne-1 (5%).

3. The behavior of the isomeric dibromides when heated or reacted with permanganate, an alcoholic alkali, or alcoholic ammoniacal silver nitrate has been investigated.

4. It has been established that when 1,4-dibromobutadiene-1,2 is heated with hydrobromic acid and Cu_2Br_2, it isomerizes, the principal product being 1,2-dibromobutadiene-1,3 (an allene-1,3-diene rearrangement) with a trace of the acetylenic dibromide.

5. It has been shown that the diene dibromide is relatively resistant to the action of an alcoholic alkali, but that it substitutes ethoxyl groups for the bromine atoms when heated for a long time. The acetylenic dibromide produces diacetylene, even in the cold, while the allene dibromide yields vinylbromoacetylene and then vinylacetylene.

6. The observed patterns of behavior have been explained on the basis of the electron theory.

LITERATURE CITED

[1] A.A.petrov, J.Gen.Chem., 8, 131, 142, 208, (1938); 9, 2232 (1939); 10, 819, 1113, 1418, 1682, 1887 (1940); 11, 661 (1941); 13, 102, 108, 155, 230, 237, 481 (1943); 15, 981 (1945); 17, 497, 539 (1947); Dokl. USSR Acad. Sci., 56, 937 (1947); A.A.Petrov and N.P.Sopov, J.Gen.Chem. 17, 1543 (1947).

[2] A.A.Petrov, Trans. Voronezh State University 10, No. 2, 101 (1938); Prog.Chem. 14, 3 (1944).

[3] I.N.Nazarov, Izv. USSR Acad.Sci., Div.Chem.Sci., 683, 1938; Prog.Chem. 14, 3, (1945). I.N.Nazarov and M.V.Kuvarzina, Izv. USSR Acad.Sci., 677 (1938); D.D.Cofman, J.Am.Chem.Soc., 57, 1978 (1935).

[4] S.V.Lebedev, A.I.Gulyayeva, and A.A.Vasilyeva, J.Gen.Chem., 5, 1421 (1935); A.L.Klebansky, L.D.Popov, and N.Ya.Tsukerman, J.Gen.Chem., 16, 2083 (1946).

[5] W.H.Carothers, G.J.Berchat and A.M.Collins, J.Am.Chem.Soc., 54, 4066 (1932); 55, 786 (1933).

[6] H.B.Dykstra, J.Am.Chem.Soc., 58, 1747 (1936).

[7] A.N.Churbakov and V.N.Ryazantsev, J.Appl.Chem. 13, 1464 (1940).

[8] A.L.Klebansky and K.K.Chevychalova, Synthetic Rubber, 4, No. 4, 5 (1935); J.H.Wernts, J Am.Chem.Soc. 57, 204 (1935).

[9] A.A.Baum, R.R.Vogt and G.F.Hennion, J.Am.Chem.Soc., 61, 1458 (1939).

[10] R.A.Jacobson, H.B.Dykstra and W.H.Carothers, J.Am.Chem.Soc., 56, 1169 (1934).

[11] J.Nieuwland and R.Vogt. The Chemistry of Acetylene. GIIL, Moscow, 1947.

[12] I.A.Rottenberg and M.A.Favorskaya, J.Gen.Chem., 6, 185 (1936).

[13] I.N.Nazarov, Prog.Chem., 14, 3 (1945).

[14] Ya.K.Syrkin and M.E.Dyatkina. Chemical Bond and Molecular Structure. State Chemical Press, 1946.

[15] K.Rengert and H.J.Schumacher, Ber., 73, 1025 (1940).

[16] A.A.Petrov, Trans. Tashkent Aviation Institute, Symposium I, 78 (1943).

[17] T.A.Favorskaya, J Gen.Chem. 9, 386 (1939); 10, 461 (1940); 12, 638 (1942).

[18] A.A.Petrov, J.Gen.Chem., 13, 237 (1943).

[19] A.A.Petrov, J.Gen.Chem. 13, 102, 108, 238 (1943); A.A.Petrov and N.P.Sopov, J.Gen.Chem. 17, 1105 (1947).

[20] R.A.Jacobson and W.H.Carothers, J.Am.Chem.Soc., 55, 4667 (1933).

[21] A.A.Petrov, J.Gen.Chem., 17, 936 (1947).

[22] I.I.Strizhevsky and M.D.Chekhover, J.Gen.Chem. 10, 1303 (1940).

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THE ADDITION OF HYDROGEN TO ACETYLENE DERIVATIVES

XLII. THE INCOMPLETE ETHERS OF AN ACETYLENIC GLYCOL

THEIR REACTIONS AND HYDROGENATION

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The paper by Yu. Zalkind and I.Khasova [1] describes the hydrogenation of the complete ethers of an acetylenic glycol: tetramethylbutynediol. The present paper deals with research on the incomplete ethers of the same glycol, viz.: the ethyl and isoamyl ethers, as well as the ethers of an acetylenic alcohol – dimethylacetylenylcarbinol. The incomplete ethers were prepared by Sh. Mamedov's method [2]; heating the glycol with the corresponding alcohol and a small quantity of sulfuric acid. The reaction product was treated with ethylmagnesium bromide dissolved in ether in order to remove the complete ether that was formed at the same time. The complete ether remained in solution, while the incomplete ether was thrown down as a mixed magnesium alcoholate. The precipitate was washed with ether, and decomposed with sulfuric acid, the resulting incomplete ether being purified by distillation. The monoethyl ether of tetramethylbutynediol is an oily liquid with a pleasant odor, which boils at 184°. The b.p. of the monoisoamyl ether is 209-210°.

When these ethers were hydrogenated with colloidal palladium in alcoholic solution, it was found that, like the complete ether, they add hydrogen somewhat more slowly than the glycol does. The increase in the molecular weight of the radical that enters the ether and the substitution of the isoamyl group for the ethyl group retard the reaction, especially when the quantity of catalyst used is small. This is seen in the subjoined data which give the time (in minutes) required for adding two atoms of hydrogen to one molecule of the ether under identical experimental conditions (0.01 mol of the substance in 50 ml of alcohol).

Quantity of palladium (mg)	2	4	6	8	10
Tetramethylbutynediol	8	–	–	–	–
Incomplete ethyl ether of the glycol	11	7	4.5	3.5	3.5
Incomplete isoamyl ether	30	9	5.5	4.5	–

It should be noted that hydrogenation was much faster than with the glycol, even though it slowed down considerably after two hydrogen atoms had been added to a molecule of the incomplete glycol. Thus, when 4 mg of palladium was used, the monoethyl ether added 77% of the four hydrogen atoms in 33 minutes, while when 6 or 8 mg of palladium

* Deceased.

was used, the triple bond was converted into a single bond within 60 and 36 minutes, respectively. With 4 mg of palladium, 77% of the monoisoamyl ether was converted into the saturated ether within 30 minutes. These results show that the glycol's incomplete ethers lie between the glycol and its complete ethers, as far as catalytic hydrogenation is concerned. Here, too, the effect of increasing the size of the ether's radical upon the rate of hydrogenation is due to an increase in the screening of the triple bond, and the less sharp break in the reaction rate after the triple bond has been converted into a double bond apparently confirms the statements concerning the possible role played by the hydrogen bond in an ethylenic glycol made by one of the present authors in a previous paper, [3].

In the presence of platinum black both of these ethers add four atoms of hydrogen per molecule of ether, the hydrogenation apparently continuing further by the reduction of the hydroxyl and alkoxy groups.

The following ethers were synthesized and identified:

$(CH_3)_2C(OC_2H_5)-C\equiv C-C(OH)(CH_3)_2$ (I)
$(CH_3)_2C(OC_2H_5)-CH=CH-C(OH)(CH_3)_2$ (II)
$(CH_3)_2C(OC_2H_5)-CH_2-CH_2-C(OH)(CH_3)_2$ (III)
$(CH_3)_2C(OC_5H_{11})-C\equiv C-C(OH)(CH_3)_2$ (IV)
$(CH_3)_2C(OC_5H_{11})-CH=CH-C(OH)(CH_3)_2$ (V)
$(CH_3)_2C(OC_5H_{11})-CH_2-CH_2-C(OH)(CH_3)_2$ (VI)

As we know, when acetylenic glycols are heated with potassium hydroxide, they decompose, forming two molecules of a ketone and acetylene. It might be supposed that under these conditions incomplete ethers would yield ethers of the acetylenic alcohols, in accordance with the following equation:

$$R_2C(OR')-C\equiv C-C(OH)R_2 \longrightarrow R_2C(OR')-C\equiv CH + R_2CO.$$

Our expectations were borne out by experiment, and we used this method to synthesize the first representatives of the ethers of acetylenic alcohols: the ethyl and isoamyl ethers of dimethylacetylenylcarbinol, as oily, fragrant liquids.

$(CH_3)_2C(OC_2H_5)-C\equiv CH$ (VII) and $(CH_3)_2C(OC_5H_{11})-C\equiv CH$ (VIII).

The ethyl ether boils at 94-95°, the isoamyl at 133-134°.

Some time ago it was found that when acetylenic alcohols are heated with cuprous chloride, they are condensed to diacetylenic glycols [4]. As an experiment made with the ethyl ether of dimethylacetylenylcarbinol showed, the ethers react similarly, forming ethers of diacetylenic glycols when heated in a current of air with cuprous chloride. We thus synthesized the diethyl ether of 2,7-dimethylocta-3,5-diyne-2,7-diol:

$$(CH_3)_2C(OC_2H_5) - C \equiv C - C \equiv C - C(OC_2H_5)(CH_3)_2 \quad (IX)$$

This is a viscous liquid with a b.p. of 91-92° at 6 mm.

EXPERIMENTAL

Synthesis of incomplete ethers of tetramethylbutynediol. Monoethyl ether (I). 14 g of tetramethylbutynediol, 32 g of ethyl alcohol, and 3 ml of sulfuric acid were heated to 75° for 5.5 hours. The mixture was then neutralized with soda, the top layer was removed, and the lower layer extracted three times with ether. The extracts were combined with the top layer, desiccated with sodium sulfate, and fractionated. Two fractions were collected: 174-184° and 184-186°. The amount of hydroxyl in the second fraction was determined by the Tserevitinov method.

0.2000 g substance: 19.4 ml ethane (17°, 738 mm).
$C_{10}H_{17}O(OH)$. Computed ethane: 28 ml.

Hence, this fraction contained 69.3% of the incomplete ether and 30.7% of the complete one. The fraction was treated with a solution of ethylmagnesium bromide to eliminate the latter. A solution prepared from 4.5 g of magnesium and 21 g of ethyl bromide, was added to 32 g of the mixture of ethers, containing 8.48 g of the glycol's diethyl ether. The next day the ethereal solution was decanted from the precipitate of the magnesium alcoholate of the incomplete ether, and the precipitate was washed repeatedly with ether and then decomposed with sulfuric acid. The substance was extracted with ether, desiccated with sodium sulfate, and distilled. This yielded two fractions: 180-183° and 184°. The second fraction was analyzed.

0.1566 g substance: 22.2 ml ethane (17.5°, 722 mm).
$C_{10}H_{17}(OH)$ Computed ethane: 23.1 ml.

d_{20}^{20} 0.8892; n_D^{20} 1.4390; MR_D 50.25.
$C_{10}H_{18}O$. Computed: MR_D 49.55.

Monoisoamyl ether of tetramethylbutynediol (IV). 14 g of the glycol, 60 g of isoamyl alcohol, and 2.5 g of sulfuric acid were heated to 85-90° for 6 hours. The usual treatment resulted in the recovery of an oil that boiled at 209-210°.

0.1566 g substance: 11.2 ml ethane (16°, 731 mm).
$C_{13}H_{23}O(OH)$. Computed ethane: 18.09 ml.

Hence, the product contained 65% of the monoether. When the product was twice treated with a solution of ethylmagnesium bromide as indicated above, we recovered an oil with a characteristic odor and a b.p. of 209-210°.

0.1502 g substance: 17.25 ml ethane (18°, 722 mm).
$C_{13}H_{23}O(OH)$. Computed ethane: 17.79 ml.
0.1400 g substance: 0.3804 g CO_2; 0.1468 g H_2O.
Found %: C 74.10; H 11.65.
$C_{13}H_{24}O_2$. Computed %: C 73.52; H 11.40.

d_{20}^{20} 0.8519; n_D^{20} 1.4420; MR_D 65.90.
$C_{13}H_{24}O_2$. Computed: MR_D 63.39.

Hydrogenation of Incomplete Ethers of Tetramethylbutynediol

For all the experiments with palladium, the catalyst was taken from the same solution, containing 1.25 mg of palladium per ml. Starch served as the protective colloid. Each test was made with 0.01 mol of the mono ether dissolved in 50 ml of alcohol. The activity of the catalyst was checked by making a test with 0.01 mol of tetramethylbutynediol; it took 8 minutes to add two atoms of hydrogen. In the tables, T denotes the test temperature; B the pressure; t the time, from the beginning of the test (in minutes); V the volume of hydrogen absorbed from the beginning of the test (in ml); and H_2 the volume of hydrogen corresponding to 2 hydrogen atoms per molecule of the substance to be hydrogenated.

Monoethyl ether (1.7 g)

Test 1. T 20°, B 733 mm, H_2 249 ml, 2 mg of palladium.

t	3	6	9	12	18	24	30
V	83	150	205	262	280	289	294
% H_2 ..	33.3	60.2	82.3	105.2			

Test 2. T 20°, B 738 mm, H_2 247.5 ml, 4 g of palladium

t	3	6	9	12	18	24	33
V	175	245	257	266	282	298	317
% H_2	70.07	98.9	103.7				

Test 3. T 20° B 738 mm, H_2 247.5 ml, 6 mg of palladium

t	3	6	15	21	27	33	60
V	200	280	345	370	390	410	492
% H_2 ..	80.8	113.					

Test 4. T 20°, B 738 mm, H_2 247.5 ml, 8 mg of palladium.

t	3	4	5	6	9	15	21	27	36
V	223	281	298	313	343	388	428	461	409
% H_2	95.4	113.8	120.						

Test 5. T 20°, B 733 mm, H_2 249 ml, 10 mg of palladium.

t	3	6	12	24	33
V	190	295	365	454	502.
% H_2	76.2	118			

Monoisoamyl ether (2.12 g).

Test 6. T 20°, B 731 mm, H_2 250 ml, 2 mg of palladium.

t	3	6	9	12	18	24	30	33
V	66	115	144	175	209	235	251	256
% H_2	26.4	45.2	57.6	70	83.6	94	100.8	

Test 7. T 20°, B 737 mm, H_2 247.8 ml, 4 mg of palladium

t	3	6	9	12	15	21	27
V	93	180	250	290	320	330	339
% H_2	37.5	72.6	100.				

Test 8. T 21°, B 735 mm, H_2 249 ml, 6 mg of palladium.

t	3	6	9	12
V	138	242	259	269
% H_2	55.4	97.1	104.5.	

Test 9. T 20°, B 737 mm, H_2 247.7 ml, 8 mg of palladium.

t	3	6	9	15	21	27
V	220	270	279	293	314	322
% H_2	88.8	109				

To ascertain how hydrogenation takes place at the single bond, we made a test with a high concentration as against the monoisoamyl ether, 1.06 g (0.005 mol) of which was taken.

Test 10. T 20°, B 731 mm, H_2 124.8 ml, $2H_2$ 249.6 ml, 8 mg of palladium

t.....	3	9	15	21	27	33	42	51
V	143	165	181	195	207	219	235	250
% $2H_2$	57.2	66	72.4	78	82.8	87.6	94	100.

Leboux-Wilstatter platinum black was prepared for hydrogenation by platinum.

Test 11. 1.7 g of the monoethyl ether, 50 ml alcohol, 0.6984 g of platinum, T 27°, B 729 mm, $2H_2$ 513.2 ml.

t	3	6	9	12	15	21	27	30
V	165	300	435	530	600	718	788	810
% $2H_2$	32.15	58.4	84.7	103.3.				

We see that hydrogenation results in the rapid addition of 6 atoms of hydrogen to a molecule of the ether, evidently by the substitution of hydrogen for the hydroxyl or ethoxyl groups or, possibly, for both of them.

Test 12. 2.12 g of the monoisoamyl ether, 50 ml of alcohol, 0.6984 g of platinum, T 27°, B 729 mm, $2H_2$ 513.2 ml.

t	3	6	9	15	21	27	36
V	138	257	340	430	473	505	536
% H_2	26	56	66	85	92	98	104.4

Thus, no discontinuity in the rate is seen after addition of two hydrogen atoms, and hydrogenation continues after conversion of the triple bond into a single bond.

Investigation of the Hydrogenation Products of the Incomplete Ethers of Tetramethylbutynediol

To isolate the hydrogenation products, the solution was diluted with ether after the reaction was complete, then the catalyst was filtered out and the solution desiccated with sodium sulfate and fractionated. The resulting incomplete ethylenic and saturated ethers were oils with pleasant odors.

Moncethyl ether of tetramethylbutynediol (II)

B.p. 181-182°; d_{20}^{20} 0.0885; n_D^{20} 1.4413; MR_D 51.10.
$C_{10}H_{20}O_2$. Computed: MR_D 51.08.

3 g of the monoethyl ether was oxidized with a solution of 5.5 g of potassium permanganate. The reaction was complete within 4 hours. After the usual treatment, acetone was found in the neutral products by the iodoform reaction. The acids were extracted with ether and converted into the ammonium, and then into the silver salts.

0.3450 g substance: 0.1510 g Ag.
Found %: Ag 43.8.
$C_6H_{11}O_3Ag$. Computed %: Ag 45.1.

The production of acetone and ethoxybutyric acid confirms the structure of the incomplete ether of tetramethylbutynediol.

Monoethyl ether of tetramethylbutanediol (III). An oil that does not decolorize bromine water. Its purification was not completed, owing to the small quantity of the substance available.

B.p. 174-176°; d_{20}^{20} 0.8622; n_D^{20} 1.4398.

0.1051 g substance: 0.2628 g CO_2; 0.1200 g H_2O.
Found %: C 68.19; H 12.65.
$C_{10}H_{22}O_2$. Computed %: C 68.89; H 12.64.
0.1288 g substance: 19.9 ml ethane (26°, 729 mm).
$C_{10}H_{21}(OH)$. Computed ethane: 18.9 ml.

Monoisoamyl ether of tetramethylbutenediol (V).

B.p. 201-202°; n_D^{20} 1.4444; d_{20}^{20} 0.8720; MR_D 65.23.
$C_{13}H_{26}O_2$. Computed: MR_D 64.95

0.0830 g substance: 0.2210 g CO_2; 0.0938 g H_2O.
0.1072 g substance: 19.8 g benzene: Δt 0.130°.
Found %: C 72.61; H 12.64; M 212.7.
$C_{13}H_{26}O_2$. Computed %: C 72.85; H 12.23; M 214.2.

Oxidation by potassium permanganate yielded acetone, identified by the iodoform reaction, and amoxyisobutyric acid, analyzed as its silver salt.

0.0318 g substance: 0.0126 g Ag.
Found %: Ag 39.6.
$C_9H_{17}O_3Ag$. Computed %: Ag 38.43.

Monoisoamyl ether of tetramethylbutanediol (VI).

B.p. 191-193°; d_{20}^{20} 0.8601; n_D^{20} 1.4436; MR_D 66.54.
$C_{13}H_{28}O_2$. Computed: MR_D 65.40.

0.1664 g substance: 0.4388 g CO_2; 0.1984 g H_2O.
Found %: C 71.9; H 13.24.
$C_{13}H_{28}O_2$. Computed %: C 72.2; H 12.96.
0.0812 g substance: 9.4 ml ethane (27°, 729 mm).
$C_{13}H_{27}O(OH)$. Computed: 9.64 ml.

The Ethers of Dimethylacetylenylcarbinol

Ethyl ether of dimethylacetylenylcarbinol (VII). 6 g of the monoethyl ether of tetramethylbutynediol and 5.6 g of powdered potassium hydroxide were slowly heated in a Wurtz flask, the reaction products being collected in a receiver. The distillate comprised two fractions. The first one distilled at 80-100°, the second consisting of the unchanged glycol ether. After the first fraction had been desiccated with calcium chloride, it distilled at 94-95°. Yield = 2.8 g (71.8% of the theoretical). A mobile, colorless, fragrant liquid, which forms a white precipitate when treated with ammoniacal silver nitrate.

d_{20}^{20} 0.8000; n_D^{20} 1.4040; MR_D 34.23. $C_7H_{12}O$. Computed: MR_D 34.17.

0.1040 g substance: 0.2878 g CO_2; 0.0964 g H_2O.
0.1536 g substance: 20.9 g benzene: Δt 0.343°.
Found %: C 75.50; H 10.38; M 109.2.
$C_7H_{12}O$. Computed %: C 74.93; H 10.84; M 112.1.
0.1492 g substance: 33 ml ethane (20°, 725 mm).
$C_7H_{11}O(H)$. Computed ethane: 33.6 ml.

The ethyl ether was hydrogenated with palladium.

Test 13. 0.56 g of the acetylenic ether (0.005 mol), 50 ml of alcohol, T 20°, B 729 mm, $2H_2$ 256.6 ml.

t	3	6	9	12
V	160	230	253	263
% $2H_2$	62.4	89.63	98.6	

Isoamylether of dimethylacetylenylcarbinol (VIII). 10.69 g of the monoisoamyl ether of tetramethylbutynediol was heated with 8.5 g of powdered potassium hydroxide over a glycerol bath. This yielded 5 g (64.4% of the theoretical) of a highly mobile liquid with a characteristic odor, which formed a white precipitate with ammoniacal silver nitrate.

d_{20}^{20} 0.8220; n_D^{20} 1.4341; MR_D 48.69. $C_{10}H_{18}O$. Computed: MR_D 48.02.

0.1430 g substance: 22.6 ml ethane (22.5°, 735 mm).
$C_{10}H_{17}O(H)$. Computed ethane: 23.5 ml.
0.0724 g substance: 0.2060 g CO_2; 0.0790 g H_2O.
Found %: C 77.60; H 12.21.
$C_{10}H_{18}O$. Computed %: C 77.92; H 11.77.

Diethyl ether of 2,7-dimethylocta-3,5-diyne-2,7-diol (IX). 3 g of the ethyl ether of dimethylacetylenylcarbinol in 60 ml of alcohol was added, with mechanical stirring and heating over a water bath, to a mixture of 15 g of cuprous chloride, 30 g of ammonium chloride, 60 ml of water, and 3 drops of hydrochloric acid. Air was passed through the mixture for 5 hours, being replaced by oxygen toward the end of that period. The solution was filtered, and the product extracted with ether, desiccated with sodium sulfate, and fractionated. This yielded 2 g of a viscous liquid (66.96% of the theoretical yield) with a b.p. of 91-92° at 6 mm.

d_{20}^{20} 0.9001; n_D^{20} 1.4794; MR_D 69.78. $C_{14}H_{22}O_2$. Computed: MR_D 66.13.

0.1088 g substance: 0.2922 g CO_2; 0.1040 g H_2O.
0.1076 g substance: 20.94 g benzene: Δt 0.116°.
Found %: C 75.0; H 10.6; M 225.9.
$C_{14}H_{22}O_2$. Computed %: C 75.61; H 9.98; M 222.2.

The product does not react with ethylmagnesium bromide.

SUMMARY

The catalytic hydrogenation of the incomplete ethers of tetramethylbutynediol has been investigated. In the presence of palladium these ethers add hydrogen more slowly than the glycol does; the reaction slows down after the triple bond has been changed into a single bond, but further hydrogenation is easier than is the case with the glycol. When the incomplete ethers of the acetylenic glycol are heated with potassium hydroxide, they break down, forming an ether of an acetylenic alcohol and a ketone – a creation that may be used as a method of synthesizing the ethers of acetylenic alcohols. The example of the ethyl ether of dimethylacetylenylcarbinol was used to show that heating ethers of acetylenic alcohols with cuprous chloride causes them to condense, forming ethers of a diacetylenic glycol.

LITERATURE CITED

[1] J.Gen.Chem., 8, 2135 (1948).

[2] S.Mamedov. Research on Glycol Ethers. Baku, 1944, p. 71, 73.

[3] Yu. Zalkind, J.Gen.Chem., 18, 2149 (1948).

[4] Yu. Zalkind and M.Aizikovich, Journal Gen.Chem., 7, 227 (1937).

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RESEARCH ON THE REACTION OF SULFUR WITH UNSATURATED COMPOUNDS

V. ACTION OF SULFUR ON MONOUNSATURATED ALIPHATIC HYDROCARBONS*

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Awarded the Order of Lenin

The reaction of sulfur with the higher homologs of ethylene has attracted the attention of many research workers.*** As early as 1886, Jacobsen [2] pointed out that unsaturated hydrocarbons react with sulfur to form sulfuration products ("thiols") and hydrogen sulfide. Later, the sulfuration of the higher olefins was studied by Friedman [3,4], Jones and Reid [5], and Brooks and Humphrey [6].**** All of these authors, whose work has been discussed in our first report [8], reached contradictory results. All of them reported, however, that when the olefins are heated with sulfur above 190°, hydrogen sulfide is liberated vigorously, which was sometimes wrongly taken to be the initial stage of the interaction between these reagents. In reality, the sulfuration of unsaturated hydrocarbons takes place at lower temperatures (120-160°), setting in even at 40° [9], though at a negligible rate, to be sure. In 1944 several reports were published [10,14], dealing with the interaction of sulfur with the monoolefins. The major goal of these researches was ascertaining the mechanism of the process of vulcanizing the rubber macromolecule and the structure of the vulcanizate, on the basis of model systems. The olefin macromolecules thus served as the models. That is why the olefins were sulfurized under vulcanization conditions, i.e., at 120-140°, with a low sulfur concentration, and, usually, with accelerators present.

Armstrong, Little, and Doak, [10] made a thorough study of the sulfuration of the olefins under these conditions. They produced various ratios of volatile and nonvolatile sulfuration products, depending upon the structure of the initial hydrocarbon and the reaction conditions. The structure of the reaction's volatile products proved

*A lecture delivered at a scientific meeting of Leningrad University, 21 November 1947.

**Deceased.

***Cf [1] for an exhaustive survey of the literature on the action of sulfur upon unsaturated compounds (more than 400 entries in the bibliography.)

****The sulfuration of olefin hydrocarbons with a view to the synthesis of products of technological interest has been the subject of numerous patents [7]

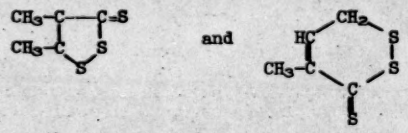
to correspond to a structure in which two molecules of the olefin are attached to one or more atoms of sulfur in the α-position to the double bond. Thus, dicrotyl sulfide (with traces of the disulfide) was formed in the sulfuration of butene-2; 2-methylbutene-2 and 2-methylbutene-1 yielded a mixture of isomeric symmetrical and asymmetrical β,γ-unsaturated sulfides and disulfides. Sulfides and disulfides of an analogous allyl structure were also recovered when sulfur was reacted with 5-methylnonene-4. It is of interest that the formation of dialkenyl sulfides and disulfides must be accompanied by the liberation of hydrogen sulfide. The authors did not find this, however, in practice. It must be supposed that the hydrogen sulfide reacts as a reducing agent, besides participating in the formation of polymers and inorganic sulfides. The latter is quite likely, since the reaction of the olefins with sulfur alone results in the formation of alkylalkenyl sulfides and polysulfides, as the authors cited assumed, and as the present paper demonstrates. Armstrong, Little, and Doak suggest a chain mechanism for the reaction of sulfur with the olefins.

These researches have been continued by Hull, Olsen, and France [11].

Farmer and Shipley [12]* have made a thorough survey of the sulfuration of olefins.

Selker and Kemp [13] investigated the sulfuration of 2-methylbutene-2 at 141.6°. They recovered liquid reaction products of the R – S_x – R type, where x varies from two to six, and R is an alkyl or alkene radical. They also recovered solid reaction products with the composition of $C_5H_6S_3$ and, apparently, $C_{10}H_{10}S_3$. The former was assigned the structure of 2,5-dithiol-3-methylthiophene, tautomeric with 2,5-dithiol-3-methylthiophane:

Selker and Kemp refer to unpublished research data by Bottcher and Luttringhaus [14], who synthesized a compound with the composition of $C_5H_6S_3$ by reacting sulfur with isoprene and suggested two possible structures for it:



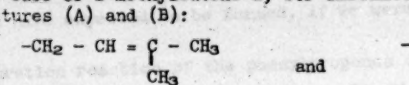
Selker and Kemp reject these suggested structures, however.

We began our research on the reaction of sulfur with unsaturated aliphatic hydrocarbons as far back as 1944, and it is not finished. The intensive work being done in this field abroad, however, and the untimely death of A.S.Broun, in whose laboratory and with whose indispensable participation our research has been conducted, compels us to publish some of our results prematurely. We have made a study of the reaction of sulfur with 2-methylbutene-2, pentene-2, and 2,3-dimethylbutene-2 under pressure and at temperatures in the neighborhood of 170°, but with no catalyst at all present; i.e., at a temperature at which the reaction takes place most rapidly but at which no hydrogen sulfide is evolved as yet. The sulfur concentration was high (the sulfur and the olefin were taken in molar concentrations ranging from 1:1 to 3:1). Heating was usually continued until all the sulfur or all the olefin had reacted.

The volatile reaction products we recovered were β,γ-mono-unsaturated sulfides, $R_1 - S_n - R_2$, where R_1 is an alkyl radical, R_2 and alkene radical, and n = 3, 2, and 1.

*Unfortunately, the paper by these authors has been inaccessible to us in the original.

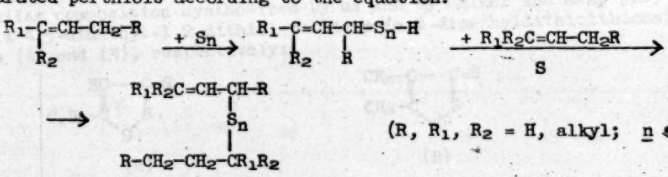
Thus, in the case of 2-methylbutene-2, for instance, R_2 may be essentially represented by the structures (A) and (B):



(A) and (B)

since oxidation of the sulfuration products yielded acetone and acetic acid. The radical R_1 is apparently tert-amyl, inasmuch as we know that, when no peroxides are present, mercaptans are added to the olefins under the influence of sulfur according to Markovnikov's rule [15,16]. The mono-unsaturation of the resultant sulfides and disulfides was proved by determining their iodine number, as well as by their analysis. As the reaction time is increased, polysulfides $R_1 - S_n - R_2$ with lower values of n, down to unity, are formed, together with β,γ-unsaturated thiols and hydrogen sulfide. The latter are also generated during the distillation of the polysulfides at ordinary pressure or at not too low pressures; they are pyrolytic decomposition products. The monosulfides are apparently also secondary reaction products, inasmuch as the lowest sulfuration products recovered in experiments made under the mildest conditions are disulfides.

We see the mechanism of the reaction involving the formation of alkylalkenyl polysulfides when sulfur reacts with the olefins as follows: In view of the conversion of the cyclic sulfur molecules into little chains with active free valencies at their ends [7] that takes place at about 160°, it may be assumed that the initial phase of sulfuration of the olefins is a free-radical reaction, involving the formation of β,γ-unsaturated perthiols according to the equation:



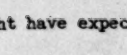
(R, R_1, R_2 = H, alkyl; $n \leqslant 8$).

Adding these perthiols to the initial olefin results in the formation of alkylalkenyl polysulfides, in which the number of sulfur atoms (n) varies with the reaction conditions. At higher temperatures, the secondary sulfuration products – monosulfides ($n = 1$) and the hydrogen sulfide formed apparently as the result of dehydrogenation of the active sulfur detached from the polysulfide bonds – predominate. The formation of the β,γ-unsaturated thiols is due to further decomposition of the monosulfides.

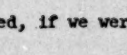
When we reacted sulfur with pentene-2 and 2-methylbutene-2, we also recovered solid reaction products, whose composition was $C_5H_8S_3$ in both instances. The formation of a substance with this formula from pentene-2 makes the structure given above for 2,5-dithiol-3-methylthiophene and proposed by Selker and Kemp [13] for compounds of this type, improbable. Moreover, when we reacted sulfur with 2,3-dimethylbutene-2, we never, under any conditions, observed the formation of a $C_8H_8S_3$ compound with the structure of:

which we might have expected to be formed, if we were to rely on the assertions of these authors.

The sulfuration reaction of the phenylpropenes discovered by us [1,18,19]:

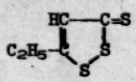


and



(R_1=H, C_6H_5; R_2 = H, CH_3, C_6H_5; R_1 or R_2 always C_6H_5), results in the smooth formation of phenylated 1,2-dithiol-3-thiones:*

These compounds, which contain the characteristic dithiolthione group > C_3S_3, have properties that resemble those of the sulfuration products of the aliphatic olefins that possess the same group (easily forming addition products with the halogens, CH_3I, and mercury salts; turns red with Grote's reagent [20]; are readily oxidized by hydrogen peroxide, yielding sulfuric acid, etc.). Hence, we may assign the structure of derivatives of 1,2-dithiol-3-thione to the sulfuration products of $C_nH_{2n-4}S_3$ olefins. Thus, the compound with the formula $C_5H_6S_3$ synthesized by us when we reacted sulfur with pentene-2 is 5-ethyl-1,2-dithiol-3-thione (α-ethyldithiolthione), while the compound with a similar composition synthesized by us and by Selker and Kemp [13] from 2-methylbutene-2 is 4,5-dimethyl-1,2-dithiol-3-thione (α,β-dimethyldithiolthione), with the structures (A) and (B), respectively:



(A)

(B)

We have already reported on the supposed mechanism of the reaction involved in the formation of dithiolthione derivatives [1,18,19].

EXPERIMENTAL

2-Methylbutene-2 was prepared by dehydrating 2-methylbutanol-2 with iodine. The olefin thus produced was washed with an alkaline solution and with water, desiccated above calcium chloride and then above sodium, and then distilled into a tower (again above sodium). The initial 2-methylbutene-2 had the following constants:

B.p. 38.3-38.5° (760.0 mm); d_4^{20} 0.6628; n_C^{20} 1.38436; n_D^{20} 1.38700; n_F^{20} 1.39321. Parachor: γ^{20} 17.39; Found: P 216.1. Computed: P 217.1 (Gibling method).

The pentene-2 was prepared by using quinoline to detach hydrogen bromide from 2-bromopentane. The resulting hydrocarbon was treated with sodium and then distilled over the latter into a tower. The initial pentene-2 had the following constants:

B.p. 35.8-36.2° (750.2 mm); d_4^{20} 0.6507; n_C^{20} 1.38183; n_D^{20} 1.38435; n_F^{20} 1.39057. Parachor: γ^{20} 17.04. Found: P 219.0. Computed: P 219.3 (Gibling method).

2,3-Dimethylbutene-2 was synthesized by dehydrating 2,3-dimethylbutanol-2 in the presence of iodine. The alcohol, in turn, was synthesized by a Grignard reaction

*According to the generally accepted nomenclature [21].

involving acetone and isopropylmagnesium chloride. The resulting olefin was washed with an alkaline solution and with water, desiccated over calcium chloride, and distilled above sodium into a tower. The initial 2,3-dimethylbutene-2 had the following constants:

B.p. 73.0-73.2° (764.0 mm); d_4^{20} 0.7080; n_C^{20} 1.40957; n_D^{20} 1.41224; n_F^{20} 1.41909. Parachor: γ^{20} 21.25. Found: P 255.2. Computed: P 254.9 (Gibling method).

The constants for the synthesized olefins cited above are in comformity with the data in the literature [22].

Research method. The initial olefins and the sulfur were used in the following molecular proportions: 1:1, 1:1.5, 1:2, and sometimes 1:3. The reaction was carried out with 40-60 g of the olefin, heated to 170 ± 5° in sealed glass tubes with the corresponding amount of sulfur. The reaction time varied from 10 to 24 hours. More than 30 tests were run in all (we shall describe only the most typical of them). When the tubes were opened, no hydrogen sulfide was liberated, as a rule, nor was any increased internal pressure found to exist. Whenever insoluble sulfuration products were produced, they were separated from the reaction mixture, chilled to -20°. Depending on the period of heating, the liquid reaction products were orange, red, or dark-hued; they did not have an unpleasant odor. The reaction mixture was treated in ethereal solution with metallic mercury in order to remove the unreacted sulfur. It should be noted that all the sulfur entered into the reaction in almost all the runs in which equimolecular or bimolecular quantities of sulfur were used, so that this latter operation proved to be superfluous. The individual sulfuration products were separated by repeated fractionation into a tower at 1-2 mm vacuum.* It was found to be more convenient, however, to perform a preliminary distillation of the reaction mixture with steam. The sulfides that distilled in this procedure were extracted with ether, desiccated above calcium chloride, and – after the ether had been driven off, vacuum fractionated into a tower. This proved to be the best procedure, inasmuch as polysulfides that had not been freed of the reaction components that are nonvolatile with steam decomposed appreciably during vacuum distillation. We measured all the physical constants of the resultant sulfides with fixed boiling points (density, refractive indexes for the C, D, and F lines, and surface tension), from which the corresponding additive molecular properties (molecular refraction and parachor) were calculated. We then determined the molecular weight, the percentages of carbon, hydrogen, and sulfur, and the iodine number.** The refractive indexes were measured with a Pulfrich refractometer; the surface tension was measured by the method of maximum bubble pressure in a device described by one of the present authors [23]. The molecular weight was determined cryoscopically in benzene; the sulfur was determined by the Gasparini method [24]; and the iodine number by the Margoshes method [25]. In order to ascertain whether it was possible to determine the unsaturation of the synthesized sulfides by measuring their iodine numbers we determined same of several synthetic saturated and β,γ-unsaturated sulfides. We found that this procedure is fully applicable to compounds containing sulfidic sulfur, which do not react with iodine under the test conditions. See [26] as well.

*We were unable to separate sulfuration products containing more than three atoms of sulfur by this method since they do not distil at the above pressure without undergoing decomposition. (The polysulfides begin to decompose at a temperature above 160°.)

**It should be pointed out that reproducible analytical data were usually obtained in different runs.

The solid volatile reaction products isolated from the reaction mixture were purified by repeated recrystallization and then identified.

Reaction Products of Mono-Olefin Sulfuration

1. Products of the Sulfuration of 2-methylbutene-2

Reacting 1: 1.5 and 1:2 molecular proportions of 2-methylbutene-2 and sulfur together for 18 to 20 hours yielded a homogeneous ruby-red liquid. 10-20% of the sulfur used and about 10% of the initial olefin did not enter into the reaction. Distillation of 121.3 g of the liquid reaction product with steam yielded 82.5 g (68% of the theoretical) of volatile sulfides. Toward the end of distillation an orange crystalline substance distilled over, which settled out of the distillate when the latter was strongly chilled. The undistilled residue weighed 19.5 g (16%). Vacuum fractionation of the volatile sulfides yielded the following constant-boiling fractions.

1. Disulfide. This substance is a yellowish liquid with an unpleasant odor. It is insoluble in alkalies. When it is oxidized with permanganate, it yields acetone, which is identified as the 2,4-dinitrophenylhydrazone with a m.p. of 128°. Acetic acid is apparently formed together with the acetone. Its presence was not reliably proved, however.

B.p. 87.5-88.0° (2 mm); d_4^{20} 0.9521; n_C^{20} 1.50158; n_D^{20} 1.50518; n_F^{20} 1.51926.
Found: MR_C 63.31; MR_D 63.69; MR_F 65.18.
$C_{10}H_{20}S_2$. Computed*: MR_C 63.70; MR_D 64.09; MR_F 65.06.

0.4382 g substance: 15.20 g benzene: Δt 0.744°.
0.7430 g substance: 15.20 g benzene: Δt 1.264°.
Found: M 198.8; 198.4.
$C_{10}H_{20}S_2$. Computed: M 204.39.

0.1164 g substance: 0.2486 g CO_2; 0.1072 g H_2O.
0.1380 g substance: 0.2949 g CO_2; 0.1216 g H_2O.
Found %: C 58.22, 58.34; H 10.30, 9.86.
$C_{10}H_{20}S_2$. Computed %: C 58.76; H 9.86.

0.1484 g substance: 0.3386 g $BaSO_4$.
0.1541 g substance: 0.3478 g $BaSO_4$.
Found %: S 31.34, 31.00.
$C_{10}H_{20}S_2$. Computed %: S 31.38.

Iodine number: found: 136.8, 138.8. $C_{10}H_{20}S_2$. Computed: 124.2.
Parachor: γ^{20} 31.03. Found: P 506.7. Computed: P 505.2 (Memford and Phillips).**

The method of synthesis, the analytical data, and the measurements of the molecular weight and the physical properties and constants of the substance indicate that it is a β,γ-unsaturated sulfide, in which the structure of the unsaturated radical is chiefly $-CH_2-CH=C(CH_3)_2$, while the saturated radical is tert-amyl.

2. Trisulfide. A dark-orange liquid with an odor that somewhat resembles that of phosgene.

B.p. 104.5-106.5° (2 mm); d_4^{20} 1.0157; n_D^{20} 1.52851; MR_D 71.75.
$C_{10}H_{20}S_3$. Computed: MR_D 72.18.
Parachor: γ^{20} 31.10: Found: P 549.9. Computed: P 554.3 (Memford and Phillips).

* The atomic increments for sulfidic sulfur were taken from Vogel [27].

** In the Memford and Phillips determination of the parachor, the atomic increment for sulfur (49.1) was taken from Vogel [27].

0.4610 g substance: 14.17 g benzene: Δt 0.758°.
0.4380 g substance: 14.40 g benzene: Δt 0.710°.
Found: M 225.3, 219.8.
$C_{10}H_{20}S_3$. Computed: M 236.46.

0.1229 g substance: 0.2298 g CO_2; 0.1002 g H_2O.
0.1362 g substance: 0.2547 g CO_2; 0.1090 g H_2O.
Found %: C 51.03, 50.99; H 9.12, 8.96.
$C_{10}H_{20}S_3$. Computed %: C 50.79; H 8.59.

0.1089 g substance: 0.3184 g $BaSO_4$.
0.1180 g substance: 0.3410 g $BaSO_4$.
Found %: S 40.15, 39.69.
$C_{10}H_{20}S_3$. Computed %: S 40.62.

Iodine number: Found: 100.8, 101.2. $C_{10}H_{20}S_3F$. Computed: 107.3.

All the data cited justify the assumption that the substance is an alkylakenyl trisulfide, with its radicals having a structure like that of the disulfide described previously.

In tests run for a longer time or at a temperature somewhat higher than 170°, the quantity of the low-boiling fractions increased, though only negligible amounts were recovered when the experiment was run under standard conditions. The following constant-boiling fractions were collected:

3. Thiol. A colorless liquid with an unpleasant, quite persistent, mercaptan odor. It is also formed (together with hydrogen sulfide) when the products of sulfurating 2-methylbutene-2 are distilled at standard pressure. It dissolves in alkalies and is recovered when the alkaline solution is acidified. It reacts with sodium, generating hydrogen, and with methylmagnesium iodide, generating methane. It decolorizes a permanganate solution instantaneously. Oxidation yields acetone, which was identified as its 2,4-nitrophenylhydrazone, with a m.p. of 127-128°. These figures indicate that the substance is an unsaturated thiol with the structure of $(CH_3)_2C{=}CH{-}CH_2SH$, possibly mixed with its isomer, $CH_3{-}CH{=}C(CH_3)CH_2SH$

B.p. 105.0-107.0° (749 mm); d_4^{20} 0.8598; n_D^{20} 1.4525; MR_D 32.60.
$C_5H_{10}S^*F$. Computed: MR_D 32.59.
Y^{20} 26.55. Found: P 269.8. Computed: P 268.1 (Memford and Phillips).

0.1163 g substance: 15.12 g benzene: Δt 0.374°.
0.1097 g substance: 14.96 g benzene: Δt 0.354°.
Found: M 105.6, 106.4.
$C_5H_{10}S$. Computed: M 102.20.

0.1202 g substance. 0.2753 g $BaSO_4$.
0.1236 g substance: 0.2836 g $BaSO_4$.
Found %: S 31.46, 31.51.
$C_5H_{10}S$. Computed %: S 31.38.

4. Sulfide. A yellowish liquid with an unpleasant odor. Insoluble in alkalies. Decolorizes a permanganate solution. These data justify the assumption that the substance is the mono-unsaturated sulfide $C_5H_9{-}S{-}C_5H_{11}$, in which the two radicals have the same structure as in the polysulfides described above.

B.p. 60-65° (3.5 mm); d_4^{20} 0.8913; n_C^{20} 1.48285; n_D^{20} 1.48615; n_F^{20} 1.49430.
Found: MR_C 55.20; MR_D 55.53; MR_F 56.32.

*The atomic increment for thiol sulfur (7.766) is taken from Mathias [28]

$C_{10}H_{20}S$F. Computed: MR_C 55.68; MR_D 56.00; MR_F 56.78.
γ^{20} 32.54; Found: P 461.8. Computed: P 456.1 (Memford and Phillips).

0.2430 g substance: 15.20 g benzene: Δt 0.453°.
0.1961 g substance: 15.38 g benzene: Δt 0.369°.
Found: M 181.1, 177.4.
$C_{10}H_{20}S$. Computed: M 172.33.

0.1829 g substance: 0.4627 g CO_2; 0.1922 g H_2O.
0.2268 g substance: 0.5762 g CO_2; 0.2473 g H_2O.
Found %: C 69.03, 69.33; H 11.76, 12.20.
$C_{10}H_{20}S$. Computed %: C 69.69; H 11.70.

0.1098 g substance: 0.1502 g $BaSO_4$.
0.1054 g substance: 0.1449 g $BaSO_4$.
Found %: S 18.80, 18.89.
$C_{10}H_{20}S$. Computed %: S 18.61.

5. 4,5-Dimethyl-1,2-dithiol-3-thione. A solid sulfuration product, which is always formed when 2-methylbutene-2 is reacted with sulfur. It settles out as acicular orange crystals when the reaction mixture is strongly chilled or when it is distilled with steam. The crystals were treated with metallic mercury in a benzene solution to eliminate the free sulfur and then purified by recrystallization from alcohol. The pure substance consists of minute yellow crystals with a m.p. of 95.5° with a disagreeable odor.

0.1022 g substance: 13.68 g benzene: Δt 0.230°.
0.1002 g substance: 14.16 g benzene: Δt 0.220°.
Found: M 166.6, 164.8.
$C_5H_6S_3$. Computed: M 162.30.

0.0642 g substance: 0.2774 g $BaSO_4$.
0.0593 g substance: 0.2568 g $BaSO_4$.
Found %: S 59.35, 59.47.
$C_5H_6S_3$. Computed %: S 59.27.

Literature data: m.p. 95.2°, according to Selker and Kemp [13].

The substance dissolves in all the usual organic solvents. It forms addition products with methyl iodide, mercury bromide, bromine, and iodine. It is oxidized to sulfuric acid by hydrogen peroxide or dilute nitric acid. It turns purplish-red when reacted with Grote's reagent [20]. The analytical data, the determination of the molecular weight, and the considerations set forth in the theoretical section of this paper indicate that the structure of the synthesized compound is 4,5-dimethyl-1,2-dithiol-3-thione:*

Nonvolatile sulfuration products of 2-methylbutene-2. Analysis and determination of the molecular weight of the higher sulfuration products, which did not distil with steam, but were soluble in benzene, yielded the following results:

0.1698 g substance: 19.00 g benzene: Δt 0.969°.
0.1102 g substance: 18.25 g benzene: Δt 0.676°.
Found: M 483.2, 458.2.

* We also recovered this same compound during the sulfuration of 2-methylbutene-1.

0.0996 g substance: 0.1632 g CO_2; 0.0559 g H_2O.
0.1044 g substance: 0.1698 g CO_2; 0.0584 g H_2O.
Found %: C 44.72, 44.40; H 6.28, 6.26.

0.1220 g substance: 0.4305 g $BaSO_4$.
0.1180 g substance: 0.4196 g $BaSO_4$.
Found %: S 48.47, 48.84.

These figures indicate that the nonvolatile sulfuration products contain more than three atoms of sulfur in the molecule. According to their average composition, they constitute an equimolecular mixture of the sulfides formed by the condensation of three or four molecules of olefins with the formula $C_{15}H_{28}S_7$ or $C_{20}H_{34}S_8$. Fractionation of the solutions of the nonvolatile reaction products yielded a fraction whose composition and molecular weight corresponded to the pentasulfide $C_{10}H_{20}S_5$.

0.1558 g substance: 16.30 g benzene: Δt 0.160°.
0.2936 g substance: 16.30 g benzene: Δt 0.299°.
Found: M 306.5, 308.0.
$C_{10}H_{20}S_5$. Computed: M 300.59.

0.1580 g substance: 0.6226 g $BaSO_4$.
0.1134 g substance: 0.4476 g $BaSO_4$.
Found %: S 54.12, 54.21.
$C_{10}H_{20}S_5$. Computed %: S 53.34.

II. Sulfuration Products of Pentene-2

Pentene-2 reacts much more readily with sulfur than does 2-methylbutene-2. Thus, when 1 mol of the olefin is reacted with 1.5 gram-atoms of sulfur for 11 hours, both constituents enter into the reaction completely. No hydrogen sulfide was evolved. The reaction product is a red-orange liquid. When it is refractionated in vacuum, about 50% by weight remains as pitch after the first distillation. The following constant-boiling fractions were recovered:

1. Disulfide. A yellowish liquid, whose properties resemble those of the disulfide prepared from 2-methylbutene-2.

B.p. 88-92° (2 mm); d_4^{20} 0.9598; n_D^{20} 1.50918; MR_D 63.60.
$C_{10}H_{20}S_2$. Computed: MR_D 64.09.
γ^{20} 33.19. Found: P 511.1. Computed: P 517.2 (Memford and Phillips).

0.3640 g substance: 17.60 g benzene: Δt 0.528°.
0.1944 g substance: 15.95 g benzene: Δt 0.309°.
Found: M 200.9, 192.9.
$C_{10}H_{20}S_2$. Computed: M 204.39.

0.1070 g substance: 0.2270 g CO_2; 0.0952 g H_2O.
0.1142 g substance: 0.2440 g CO_2; 0.1004 g H_2O.
Found %: C 57.90, 58.30; H 9.95, 9.84.
$C_{10}H_{20}S_2$. Computed %: C 58.76; H 9.86.

0.2572 g substance: 0.6000 g $BaSO_4$.
0.1662 g substance: 0.3862 g $BaSO_4$.
Found %: S 32.04, 31.92.
$C_{10}H_{20}S_2$. Computed %: S 31.38.

2. Trisulfide. An orange liquid with an odor and properties resembling the trisulfide prepared from 2-methylbutene-2. It contains about 25% of lead-blackening sulfur.

B.p. 102.0-102.2° (2 mm); d_4^{20} 1.0301; n_C^{20} 1.53881; n_D^{20} 1.54351; n_F^{20} 1.55634.

Found: MR_C 71.90; MR_D 72.42; MR_F 73.83.
$C_{10}H_{20}S_3F$. Computed: MR_C 71.71; MR_D 72.18; MR_F 73.34.
f^{20} 32.79. Found: P 549.4. Computed: P 556.8 (Sedgen).

0.3061 g substance: 17.65 g benzene; Δt 0.386°.
0.6071 g substance: 17.65 g benzene; Δt 0.776°.
Found: M 230.5, 227.4.
$C_{10}H_{20}S_3$. Computed: M 236.46.

0.1128 g substance: 0.2104 g CO_2; 0.0882 g H_2O.
0.1362 g substance: 0.2544 g CO_2; 0.1033 g H_2O.
Found %: C 50.90, 50.99; H 8.75, 8.49.
$C_{10}H_{20}S_3$. Computed %: C 50.79; H 8.59.

0.1162 g substance: 0.3398 g $BaSO_4$.
0.1166 g substance: 0.3405 g $BaSO_4$.
Found %: S 40.16, 40.11.
$C_{10}H_{20}S_3$. Computed %: S 40.62.

3. 5-Ethyl-1,2-dithiol-3-thione. This was isolated from the fractions that boil above 103° (2 mm) by freezing and subsequent recrystallization from alcohol. Minute acicular yellow crystals with a disagreeable odor; m.p. 96.0-96.5°. Its properties resemble those of 4,5-dimethyl-1,2-thiol-3-thione.

0.0250 g substance: 15.10 g benzene: Δt 0.054°.
0.0494 g substance: 15.10 g benzene: Δt 0.107°.
Found: M 157.5, 157.0.
$C_5H_6S_3$. Computed: M 162.30.

0.0299 g substance: 0.1299 g $BaSO_4$.
0.0256 g substance: 0.1119 g $BaSO_4$.
Found %: S 59.67, 60.07.
$C_5H_6S_3$. Computed %: S 59.27.

III. Sulfuration Products of 2,3-Dimethylbutene-2

2,3-Dimethylbutene-2 reacts with sulfur very readily, the principal reaction product being a trisulfide. Thus, both constituents entered completely into reaction after 1 mol of the olefin had been heated with 2 gram-atoms of sulfur for only 6 hours. This resulted in the formation of a homogeneous red-orange liquid. Practically no hydrogen sulfide was evolved. Fractionation of the reaction products in vacuum succeeded in yielding only one constant-boiling fraction, corresponding to a trisulfide. We were unable to isolate any crystalline reaction products in any of the 7 experiments we made under various conditions.

1. Trisulfide. An orange liquid. Its properties resemble those of the two trisulfides previously described.

B.p. 122.5-123.5° (2.5 mm); d_4^{20} 1.0121; n_D^{20} 1.53550. Found: MR_D 81.42.
$C_{12}H_{24}S_3F$. Computed: MR_D 81.42.

0.1252 g substance: 16.05 g benzene: Δt 0.153°.
0.1167 g substance: 16.22 g benzene: Δt 0.143°.
Found: M 261.6, 258.0.
$C_{12}H_{24}S_3$. Computed: M 264.51.

0.1094 g substance: 0.2876 g $BaSO_4$.
0.1153 g substance: 0.3023 g $BaSO_4$.
Found %: S 36.10, 36.01.
$C_{12}H_{24}S_3$. Computed %: S 36.37.

2. Thiol. This is formed when the products of the sulfuration of 2,3-dimethylbutene-2 are distilled at ordinary pressure. Distillation is accompanied by the copious evolution of hydrogen sulfide and considerable carbonization. Fractionation of the pyrolysis products yielded a narrow fraction, possessing the following constants:

B.p. 135.5-136.5° (757.6 mm); d_4^{20} 0.8766; n_D^{20} 1.4802; n_D^{13} 1.4825.
Found: MR_D 37.68. $C_6H_{12}S$. Computed: MR_D 37.21.

0.1001 g substance: 14.92 g benzene: Δt 0.291°.
0.1243 g substance: 16.02 g benzene: Δt 0.338°.
Found: M 118.2, 117.8.
$C_6H_{12}S$. Computed: M 116.22.

0.1163 g substance: 0.2313 g $BaSO_4$.
0.1137 g substance: 0.2311 g $BaSO_4$.
Found %: S 27.30, 27.27.
$C_6H_{12}S$. Computed %: S 27.59.

A colorless liquid with a disagreeable mercaptan odor. It exhibits all the chemical reactions typical of the mercaptans. With nitrous acid, it first turns greenish, and then red.

This reaction indicates that the sulfhydryl group is attached to the third carbon atom, which enables us to assign the following mercaptan structure of 2,3-dimethylbutene-1-thiol-3:

$(CH_3)_2$-CSH-C(CH_3)=CH_2.

A much smaller quantity of another mercaptan fraction with a b.p. of 140-144° (762 mm) and n_D^{20} 1.5002, possessing similar chemical properties, was likewise recovered.

0.0760 g substance: 14.80 g benzene: Δt 0.221°.
0.1512 g substance: 14.80 g benzene: Δt 0.437°.
Found: M 119.1, 119.9.
$C_6H_{12}S$. Computed: M 116.22.

0.0532 g substance: 0.1081 g $BaSO_4$.
0.0612 g substance: 0.1247 g $BaSO_4$.
Found %: S 27.92, 27.99.
$C_6H_{12}S$. Computed %: S 27.59.

Its reaction with HNO_2 at the instant of its formation (red coloration) justifies the assumption that this mercaptan is apparently 2,3-dimethylbutene-2-thiol-1: $(CH_3)_2C$=C$(CH_3)CH_2SH$.

SUMMARY

A study has been made of the reaction of sulfur with 2-methylbutene-2, pentene-2, and 2,3-dimethylbutene-2 at 170°. The reaction proceeds with the formation of liquid sulfides of the R_1-S_n-R_2 type, in which R_1 is an alkyl group, R_2 is an alkenyl group with a double bond at the β,γ-position, and n varies from 1 to 6. Chiefly disulfides (n = 2) and trisulfides (n = 3) were isolated and identified. Monosulfides (n = 1), thiols of the type R_2-SH, and hydrogen sulfide are the secondary products of the

reaction. The examples of 2-methylbutene-2 and pentene-2 have been used to show that crystalline derivatives of a 1,2-dithiol-3-thione:

are formed in the sulfuration of olefins of the R-CH=C(CH_3)-R' or R-CH_2-C(R)=CH_2 (R,R' = H, alkyl), type, in addition to the sulfides already mentioned.

LITERATURE CITED

[1] M.G.Voronkov, Vestnik of Leningrad University, No. 2, 146 (1948).

[2] E.Jacobsen, German Patent 38416 (1886); Ber., 20, 181 R (1887).

[3] W.Friedman, Petroleum, 11, 693 (1916).

[4] W.Friedman, Ber., 49, 1551 (1916).

[5] S.O.Jones, E.E.Reid, J.Am.Chem.Soc., 60, 2452 (1938).

[6] B.T.Brooks, Humphrey, Ind.Eng.Chem., 8, 746 (1917).

[7] Dr. Alexander Posnansky, Danish Patent 51564 (1935); British Patent 453921, (1935); Zbl. 1936 II. 1628; 1937, I, 2278; R.C.Wulf, U.S.Patent 1890310 (1932); Chem.Abs., 27, 515 (1933); Thiophen Products Co., U°S°Patent 1877478 (1932); Zbl., 1933, I, 508; O.E.Dietzel, German Patent 708840, (1941); Chem.Abs., 37, 3204 (1943); H.A.Gardner, U.S.Patent 1446039 (1923); Kunststoffe, 15, 26 (1925); Zbl., 1923, IV 303; E.C.Knowles, F.C.McCoy, U.S.Patent 2337473 (1943); Chem.Abs., 38, 3833 (1944); I.G.Farbenindustrie, A.G. British Patent 360993 (1930); 361356 (1931); Zbl, 1932, I, 870; 1932, II, 948; W.A.Lazier, F.K.Signaigo, J.H.Werniz, U.S.Patent 2402643 (1946); Chem. Abs., 40, 5764 (1946); F.K.Signaigo, U.S.Patent 2402456 (1946); Chem.Abs., 40, 5767 (1946); G.Pritzker, Nat. Petroleum News, 37, 871 (1945).

[8] A.S.Broun and M.G.Voronkov, J.Gen.Chem. 17, 1162 (1947).

[9] D.Spence, J.Jong, Koll.Z. 13, 265 (1913).

[10] R.T.Armstrong, J.R.Little, K.W.Doak, Ind.Eng.Chem., 36, 628 (1944).

[11] C.M.Hull, S.R.Olsen, W.C.France, Ind.Eng.Chem., 38, 1282 (1946).

[12] E.H.Farmer, F.W.Shipley, J.Polymer Sci., I, 293 (1946); Chem.Abs., 40, 6873 (1946).

[13] M.L.Selker, A.R Kemp., Ind.Eng.Chem., 39, 895 (1947).

[14] B.Bottcher, A.Luttringhaus, OPB Report, 1707, (1944).

[15] R.F.Naylor, J. polymer Sci., 1, 305 (1946); Chem.Abs., 40, 6873 (1946).

[16] W.Malisoff, E.Marks, F.Hess., Chem.Rev., 7, 498 (1930).

[17] R.Fanelli, Ind.Eng.Chem., 38, 39 (1946).

[18] M.G.Voronkov and A.S.Broun, Dokl. USSR Acad.Sci., 59, 1437 (1948).

[19] M.G.Voronkov,A.S.Broun, G.B.Karpenko, J.Gen.Chem. 19, 1927 (1949).

[20] Grote, J.Biol.Chem., 93, 25 (1931).

[21] A.M.Patterson, L T.Capelle. The Ring Index. New York, 1940, 43.

[22] G.Egloff, Physical Constants of Hydrocarbons, V.I, New York (1939).

[23] M.G.Voronkov, Industrial Laboratories, 13, 240 (1947).

[24] H.Meyer. Analysis and Determination of the Structure of Organic Substances. ONTI [United Science and Technical Press], Kiev., p. 157-158, 162, 163.

[25] U.S.S.R. Standard 2070-43.

[26] M.L.Selker, A.R.Kemp., Ind.Eng.Chem., 36, 22 (1944); S.R.Olsen, C.M.Hull, W.G. France, Ind.Eng.Chem., 38, 1273 (1946).

[27] A.I.Vogel, D.M.Cowan, J.Chem.Soc., 1943, 16.

[28] S.Mathias, Ann. Acad. Brasil.Cienc., 18, 23 (1946); Chem.Abs., 40, 6311 (1946).

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RESEARCH ON THE SESQUITERPENE ALCOHOL PALUSTROL FROM THE ETHEREAL OIL OF THE WILD ROSEMARY LEDUM PALUSTRE L.

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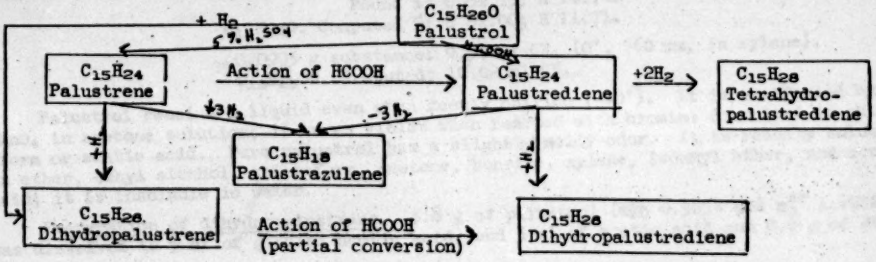
Palustrol was first discovered in the ethereal oil of the wild rosemary Ledum palustre L. in 1948 [1]. According to our research data, palustrol is a saturated alcohol, $C_{15}H_{26}O$, with a b.p. of 275-277°, which readily splits off water when acted on by acids, thus indicating that it is a tertiary alcohol. Dehydration of palustrol by various dehydrating agents results in the formation of different hydrocarbons. For instance, boiling palustrol with 90% formic acid yields the hydrocarbon palustrediene, $C_{15}H_{24}$, with two double bonds. On the other hand, heating palustrol dissolved in ethyl alcohol with 5-7% sulfuric acid results in the formation of the hydrocarbon palustrene, $C_{15}H_{24}$, with one double bond. We demonstrated the formation of palustrene and palustrediene by measuring their molecular refraction and confirmed it by synthesizing the dihydro and tetrahydro derivatives of these hydrocarbons. The saturation and composition of palustrol, together with the composition and the properties of palustrene and palustrediene, make it quite probable that palustrol is a tricyclic alcohol, the most stable element in the tricyclic structure being the bicyclo system consisting of a five-membered ring and a seven-membered ring [2]. The latter conclusion is reinforced by the fact that the dehydrogenation of palustrene and palustrediene with selenium readily resulted in the formation of a violet liquid – palustrazulene, $C_{15}H_{18}$, which forms a picrate with picric acid that fuses at 118-119°. Up to the present time we have been unable to establish conclusively the nature of the third ring (which may well be a cyclopropane, in view of the ease with which it can be ruptured). The various conversions of palustrol are illustrated in the subjoined diagram.



The following singularities in the transformations of palustrol and its derivatives are worthy of note. For instance, when palustrol is hydrogenated in acetic acid, all of it is converted into dihydropalustrene (a reaction that is apparently the result of the detachment of water from the alcohol and the addition of hydrogen to the nascent hydrocarbon). Furthermore, palustrene – a hydrocarbon with a single double bond – is smoothly converted into palustrediene – a hydrocarbon with two double bonds – by boiling with formic acid, but under these conditions dihydropalustrene is only partially (not over 30%) converted into dihydropalustrediene.

Finally, let us point out one more peculiarity. Whereas the unsaturated hydrocarbons (palustrene, palustrediene, and dihydropalustrediene) turn an intense violet when treated with bromine dissolved in chloroform or acetic acid, the saturated hydrocarbons (dihydropalustrene and tetrahydropalustrediene) exhibit no such reaction, even though they retain the azulenic bicyclo system, a proof of which is the fact that they give rise to azulene derivatives when dehydrogenated. In conclusion, let us point out that the palustrol used in the present investigation was obtained from the oil extracted from the leaves of the wild rosemary growing in the environs of Leningrad. The leaves were gathered and the oil prepared in June, 1948. Our investigation of palustrol and the other constituents of the oil is being continued.

EXPERIMENTAL

Production of palustrol. The oil of wild rosemary was chilled to -20°. The pasty product was suction-filtered at 50-80 mm. The oil, which did not yield a crystalline product (ledol) even when deeply chilled, was distilled in vacuum, a fraction with a b.p. of 120-130° (3 mm); d_{20}^{20} 0.9631; n_D^{20} 1.4930, containing 93-97% of the alcohol being collected. To eliminate any impurities of an unsaturated nature, the fraction was dissolved in freshly distilled acetone and oxidized with potassium permanganate until it no longer caused any decolorization of the latter (palustrol itself is unaffected by $KMnO_4$). The manganese dioxide was filtered out, the acetone driven off, and the oil washed with water, distilled with steam, and then distilled in vacuum. This yielded a colorless oil with the following properties.

B.p. 275-277° (with decomposition), 129-131° at 2-3 mm;
d_{20}^{20} 0.9654; n_D^{20} 1.4920; n_D^{22} 1.4912; α_D^{18} – 17.6°; MR_D 66.67.

$C_{15}H_{26}O$. Computed: MR_D 66.39.

In some instances samples of palustrol were obtained with somewhat different properties. The properties cited above are apparently characteristic of the purest palustrol. The yield of palustrol from the oil reached 50% at times, but usually was 30-40%.

0.1367 g substance: 0.4068 g CO_2; 0.1445 g H_2O.
Found %: C 81.15; H 11.74.
$C_{15}H_{26}O$. Computed %: C 81.08; H 11.71.

0.0993 g substance: 9.97 ml CH_4 (0°, 760 mm, in xylene).
$C_{15}H_{25}OH$. Computed: 10.02 ml CH_4.

Palustrol remains a liquid even when deeply chilled (-40°). It is unaffected by $KMnO_4$ in acetone solution; it turns violet when reacted with bromine dissolved in chloroform or acetic acid. Pure palustrol has a slightly moldy odor. It is readily soluble in ether, ethyl alcohol, chloroform, acetone, benzine, xylene, isoamyl ether, and acetic acid; it is insoluble in water.

Preparation of dihydropalustrene. 3.8 g of palustrol (d_{20}^{20} 0.9654 and n_D^{22} 1.4912) was dissolved in 5 ml of glacial acetic acid, and 3 ml of acetic acid and 0.8 g of PtO_2

previously reduced with 165 ml of H_2, were added to the mixture. Hydrogenation is extremely slow. 381 ml of H_2 was added during 35 hours. At the end of hydrogenation there were two layers in the reaction flask. The acetic acid was neutralized by soda, and the neutral solution was distilled with steam. This yielded a hydrocarbon, the constants of which were as follows after redistillation over sodium:

B.p. 112-115° (8-10 mm). n_D^{20} 1.4853; d_{20}^{20} 0.9068; MR_D 65.11.
$C_{15}H_{28}$. Computed: MR_D 64.87.

0.1244 g substance: 0.3982 g CO_2; 0.1408 g H_2O.
Found %: C 87.29; H 12.57.
$C_{15}H_{28}$. Computed %: C 87.38; H 12.62.

Dihydropalustrene does not react with bromine or potassium permanganate.

Dehydration of palustrol by 5% sulfuric acid. 15 g of the palustrol was dissolved in 35 ml of absolute ethyl alcohol, and 2 ml of H_2SO_4 (d = 1.84) in 5 ml of alcohol was poured into the solution. The mixture was heated over a water bath until boiling set in. It turned red, and then changed to violet. When the solution was chilled, 8.5 ml of a flaking oil was recovered. Reheating of the mixture yielded another 5 ml of the yellow-green oil. The total recovered was 13.5 ml. Sometimes this operation is completed successfully with a single heating, particularly when the sulfuric-acid concentration is 7%. The oil was driven off with steam. The recovered oil was distilled in vacuum over sodium. This yielded a colorless hydrocarbon, with properties that differ slightly from those previously known [1]:

B.p. 96-100° (2 mm); 100-103° (3 mm); 253-256° (762 mm); d_{20}^{20} 0.9243; n_D^{20} 1.4975; α_D^{19} + 42.12° (+ 10.53° in a 2.5-cm tube); MR_D 64.64.
$C_{15}H_{24}$. Computed: MR_D 64.403.

0.1246 g substance: 0.4021 g CO_2; 0.1315 g H_2O.
Found %: C 88.01; H 11.73.
$C_{15}H_{24}$. Computed %: C 88.23; H 11.77.

When palustrene is distilled at atmospheric pressure, its properties change (d_{20}^{20} 0.9173 and n_D^{20} 1.4987), possibly because of isomeric transformations. Palustrene readily decolorizes $KMnO_4$ dissolved in acetone. It is colored violet by bromine in chloroform or acetone solution. It is readily soluble in chloroform, acetone, and benzine, but poorly soluble in alcohol or acetic acid; it is insoluble in water.

Hydrogenation of palustrene. 5.69 g of palustrene (n_D^{22} 1.4970 and d_{20}^{20} 0.925) was hydrogenated with 0.5 g of PtO_2 (Adams method), previously reduced by 86.5 ml of H_2 in 10 ml of CH_3COOH. The palustrene added 635 ml of H_2 (24°, 762 mm) during 1 hour and 45 minutes. The hydrogenation rate was 30-50 ml per 5 minutes. Then the consumption of hydrogen sharply dropped to 7 ml of H_2 and less in 5 minutes. A total of 710 ml of H_2 was consumed, 1 double bond requiring 625 ml (0°, 760 mm). The solution was neutralized, and the colorless oil distilled with steam and then with Na in vacuum.

d_{20}^{20} 0.9036; n_D^{20} 1.4852; α_D^{19} + 5.44° (+1.36° in a 2.5 cm tube); MR_D 65.36.
$C_{15}H_{28}$. Computed: MR_D 64.87.

Before analysis, the dihydropalustrene was double distilled over Na at a b.p. of 91-94° (2-3 mm).

0.1318, 0.1275 g substance: 0.4213; 0.4078 g CO_2; 0.1520, 0.1463 H_2O.
Found %: C 87.17, 87.23; H 12.81, 12.74.
$C_{15}H_{28}$. Computed %: C 87.38; H 12.62.

Dihydropalustrene does not decolorize permanganate in acetone solution; it does not react with bromine.

Action of 90% formic acid upon palustrol. Synthesis of palustrediene. 10 g of palustrol was heated to a gentle boil with 20 ml of 90% formic acid for 15 minutes. Then the formic acid was neutralized with a dilute soda solution (or with NaOH, which does not affect the result), and the oil distilled with steam.

The resultant greenish oil (yield = 8.5 g) had the following properties: d_{20}^{20} 0.9073; n_D^{20} 1.4996; the oil was colorless after it was distilled over Na:

B.p. 251-253° (763 mm); d_{20}^{20} 0.9038; n_D^{20} 1.4992; α_D^{18} from + 5° to + 21.4°; MR_D 66.29. $C_{15}H_{24}F_2$. Computed: MR_D 66.13.

0.1196 g substance: 0.3854 g CO_2; 0.1256 g H_2O.
Found %: C 87.88; H 11.67.
$C_{15}H_{24}$. Computed %: C 88.23; H 11.77.

Palustrediene is colored violet by bromine in a chloroform or acetic-acid solution. It readily decolorizes $KMnO_4$ dissolved in acetone.

Hydrogenation of palustrediene. Synthesis of tetrahydropalustrediene. 0.2 g of PtO_2 (Adams method) was hydrogenated in 10 ml of glacial acetic acid. It added 62.5 ml of H_2. 3.84 g of palustrediene was poured into the mixture; a blue solution was formed. Hydrogenation lasted 5 hours, and 860 ml of H_2 was consumed. At the start the hydrogenation rate was 50-60 ml of H_2 in 10 minutes, but after 440 ml had been added (one double bond requires 421.5 ml of H_2), the hydrogenation rate was cut in half, and toward the end of the hydrogenation, the rate was 2-3 ml of H_2 in 10 minutes. After the theoretical quantity of H_2 had been added to the two double bonds, the solution was neutralized, and the oil distilled with steam. This yielded a colorless oil (d_{20}^{20} 0.8810; n_D^{20} 1.4773). Distillation over Na yielded:

B.p. 241-243° (759 mm); d_{20}^{20} 0.8803; n_D^{20} 1.4773; α_D^{19} +3.2°; MR_D 66.79. $C_{15}H_{28}$. Computed: MR_D 67.07.

0.1258 g substance: 0.3972 g CO_2; 0.1501 g H_2O.
Found %: C 86.65; H 13.25.
$C_{15}H_{28}$. Computed %: C 86.54; H 13.46.

In contrast to palustrediene, tetrahydropalustrediene does not exhibit a color reaction with bromine (in chloroform or acetic acid), but it does form a blue-violet dehydrogenation product when dehydrogenated with selenium, i.e., it contains an azulene 2-ring system.

Hydrogenation of palustrediene. Synthesis of dihydropalustrediene. 1.67 g of palustrediene in 5 ml of glacial acetic acid was hydrogenated with 187 ml of hydrogen (allowing for one double bond) in the presence of 0.1 g of platinum black. Hydrogenation was complete within 45 minutes. After neutralization, the oil was distilled with steam and then distilled over metallic sodium.

B.p. 104-106° (7-8 mm); d_{20}^{20} 0.8855; n_D^{20} 1.4834; α_D^{18} -5.12°; MR_D 66.48. $C_{15}H_{28}F$. Computed: MR_D 66.603.

0.1146 g substance: 0.3664 g CO_2; 0.1294 g H_2O.
Found %: C 87.19; H 12.54.
$C_{15}H_{28}F$. Computed %: C 87.38; H 12.62.

Dihydropalustrediene decolorizes permanganate and exhibits a color reaction (violet) with bromine in chloroform.

Action of 90% formic acid on palustrene. The palustrene used for this experiment had a d_{20}^{20} 0.9268; n_D^{20} 1.4978; α_D^{19} + 42.4°. When the palustrene was heated with the same volume of 90% formic acid, the mixture turned blue, but ended up brown. Fifteen minutes later the solution was neutralized and distilled with steam. This yielded a brown-green hydrocarbon, which was distilled in vacuum over Na and recovered in a colorless state.

d_{20}^{20} 0.9028; n_D^{20} 1.4986; α_D^{19} +12.0°; MR_D 66.30.

$C_{15}H_{24}$. Computed: MR_D 66.136.

0.1216 g substance: 0.3927 g CO_2; 0.1281 g H_2O.

Found %: C 88.07; H 11.70.

$C_{15}H_{24}$ Computed %: C 88.23; H 11.77.

The properties and the composition of the synthesized hydrocarbon do not differ from those of palustrediene, in other words, palustrene is converted into palustrediene by the action of formic acid.

Action of formic acid on dihydropalustrene. A mixture of 3.5 g of dihydropalustrene and 6 ml of 90% formic acid was heated for 15 minutes to a gentle boil. The mixture turned red, and then blue. After it had cooled, neutralizing it with soda and distilling it with steam yielded 3.9 ml of an oil (d_{20}^{20} 0.8969; n_D^{20} 1.4866; α_D^{19} -8.7°). Reheating the oil with formic acid caused practically no change in its properties. Evidently, we did not get 100% conversion to dihydropalustrediene, the constants of which are d_{20}^{20} 0.888; n_D^{20} 1.4851.

This conclusion was corroborated by hydrogenation. Catalytic hydrogenation of 1.69 g of the oil with 0.3 g of platinum black resulted in the addition of 69 ml of H_2 (instead of the 182 ml called for by the theoretical calculations). The synthesized hydrocarbon had the following properties: d_{20}^{20} 0.8996; n_D^{20} 1.4847; α_D^{19} -6.92°, i.e., its properties differ from those of tetrahydropalustrediene (d_{20}^{20} 0.881; n_D^{20} 1.4773; α_D^{19} + 3.2°). Hence, it may be considered as established that when formic acid reacts with dihydropalustrene, the double bond is not formed as readily as is the case in palustrene.

Dehydrogenation of palustrediene: 10 g of palustrediene was heated to 250-260° with 10 g of selenium. The mixture rapidly turned violet. Four or five hours later the mixture was distilled with steam, the resultant violet oil dissolved in benzine at 70-80°, and the benzine solution repeatedly shaken up with 60% sulfuric acid until the benzine solution was decolorized. The sulfuric-acid extracts (about 50 ml) were washed twice with pure benzine and then poured into 200 ml of cold water, and the oil that separated out was extracted with freshly distilled ethyl ether. The ether was driven off, the oil redistilled with steam and extracted with ether, the ether solution desiccated, and the ether driven off. The oil was dissolved in a small quantity of ethyl alcohol and an alcoholic solution of picric acid added to the solution (on the basis of 1 g of picric acid per gram of the violet oil). A pasty mass of dark needles was formed almost instantaneously. After recrystallization from alcohol, the picrate's m.p. was 118-119°. The palustrazulene picrate was decomposed by distillation with steam in the presence of an alkali. This yielded palustrazulene, which was purified by redistillation with steam and then in vacuum. The yield was 5-7%:

B.p. 133-137° (3 mm); d_{20}^{20} 0.9747.

0.1285, 0.1269 g substance: 0.4275, 0.4220 g CO_2; 0.1081, 0.1069 g H_2O.

Found %: C 90.71, 90.69; H 9.34, 9.35.

$C_{15}H_{18}$. Computed %: C 90.9; H 9.1.

Dehydrogenation of palustrene. The palustrene was dehydrogenated by the method used to dehydrogenate palustrediene. This yielded the picrate of azulene, with a m.p. of 118-119° (from alcohol), which exhibited no depression when fused in a mixed test sample with the palustrazulene picrate previously described.

SUMMARY

1. A saturated tricyclo, sesquiterpene alcohol, palustrol, $C_{15}H_{26}O$, with a b.p. of 275-277°; d_{20}^{20} 0.9654; n_D^{20} 1.4920; α_D^{19} -17.6°, after adequate purification, has been isolated from the ethereal oil of the wild rosemary Ledum palustre L.

2. When palustrol is reacted with 5% sulfuric acid, the hydrocarbon palustrene, $C_{15}H_{24}$, with one double bond and a b.p. of 253-256°; d_{20}^{20} 0.9243; n_D^{20} 1.4975; α_D^{19} +42.12°, is formed.

3. Boiling palustrol or palustrene with formic acid yields the hydrocarbon palustrediene, $C_{15}H_{24}$, with two double bonds: b.p. 251-253°; d_{20}^{20} 0.9038; n_D^{20} 1.4992; α_D^{16} +5° to + 21.4°.

4. The formation of palustrene and palustrediene from palustrol was proved refractometrically and confirmed by the synthesis of the dihydro and tetrahydro derivatives of these hydrocarbons.

5. Palustrol, plaustrene, and palustrediene all possess an azulene two-ring system, inasmuch as their dehydrogenation with selenium yields palustrazulene, $C_{15}H_{18}$, whose picrate's m.p. is 118-119°.

LITERATURE CITED

[1] N.P.Kiryalov, Dokl. USSR Acad. Sci., 60, 2 (1948).

[2] N.P.Kiryalov, Priroda [Nature], No. 8 (1946).

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THE CATALYTIC DEHYDRATION OF 2-BUTYNE-1,4-DIOL WITH AMMONIA AND WITH HYDROGEN SULFIDE. THE CATALYTIC DEHYDRATION OF CIS-2-BUTENE-1,4-DIOL

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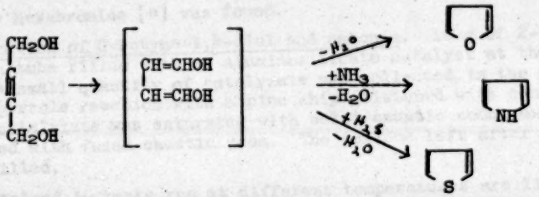
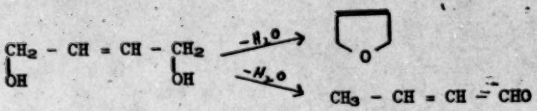
In 1939, one of the present authors [1] showed that when butane-1,4-diol was catalytically dehydrated with ammonia or hydrogen sulfide, pyrrolidine or thiophan, respectively, was formed. The present paper deals with the catalytic dehydration of two unsaturated 1,4-diols: one acetylenic (2-butyne-1,4-diol) and the other ethylenic (2-butene-1,4-diol), and with the catalytic dehydration of one of them (the butynediol) with ammonia and with hydrogen sulfide.

It has been established that passing 2-butyne-1,4-diol over alumina at 400° results in the formation of traces of furan and gaseous reaction products that contain acetylene. The catalytic dehydration of 2-butyne-1,4-diol by ammonia and by hydrogen sulfide at 400° results in the formation of pyrrole and thiophene, respectively:



As for the dehydration of 2-butene-1,4-diol, we know that the action of dilute sulfuric acid upon cis-2-butene-1,4-diol results in the formation of dihydrofuran (35%) and crotonaldehyde (65%); dehydration of trans-2-butene-1,4-diol yields nothing but crotonaldehyde. This cis-trans isomerism is like that of the glycols, but what is not like the degree of substitution in the glycols is the factor responsible for the formation of dihydrofuran compounds [2]. What is not clear, however, is this: is the crotonaldehyde formed directly from the cis form, or is the cis form first isomerized (by the hydrogen ions) to the trans form.

In the present research, cis-2-butene-1,4-diol was dehydrated with aluminosilicate, the reaction products being: dihydrofuran (yield 33.5%) and crotonaldehyde (yield 23%); the crotonaldehyde being apparently produced directly from the cis-2-butene-1,4-diol.



EXPERIMENTAL

1. Catalytic dehydration of 2-butyne-1,4-diol. 10 g of 2-butyne-1,4-diol was passed over alumina at 400° in a current of nitrogen at the rate of 6-8 drops per minute (from a dropping funnel fitted with a heating element). The receiver, chilled with an ice-salt mixture, was connected to a wash bottle containing an Ilosvay solution [3]; by the end of the run, the bottle contained a voluminous cherry-red precipitate, which indicated the presence of acetylene in the resulting gases. 2 ml of water and several drops of a dark-green oily liquid were collected in the receiver; this liquid exhibited a furan reaction with a pine chip moistened with concentrated hydrochloric acid; the catalyst was covered with a continuous black coating of carbon deposits.

10 g of 2-butyne-1,4-diol; rate of recovery 6-8 drops per minute; temperature 350°; current of nitrogen. The receiver, chilled with an ice-salt mixture, was connected to two wash bottles plunged in a freezing mixture, each containing 30 ml of a 35% solution of bromine in chloroform. After the output gases had passed through the wash bottles containing bromine, they were collected in a gasometer, and then passed through the same wash bottles three more times to achieve complete absorption of the acetylene; the slight quantity of tetrabromoacetylene produced had the following constants after double distillation:

B.p. 106-107° (10 mm); n_D^{20} 1.6228; d_4^{20} 2.8900.

Literature data for tetrabromoacetylene: Wiegman [4]; n_D^{20} 1.6326; d_4^{20} 2.9672; Peterson and Thomson [5]; B.p. 117° (14 mm); d_4^{20} 2.9638.

No solid diacetylene hexabromide [6] was found.

2. Joint dehydration of 2-butyne-1,4-diol and ammonia. 10 g of 2-butyne-1,4-diol was passed through a tube filled with an aluminosilicate catalyst at the rate of 6 drops per minute. A small quantity of catalyzate was collected in the receiver; it exhibited a marked pyrrole reaction with a pine chip moistened with concentrated hydrochloric acid. The catalyzate was saturated with solid caustic soda, extracted with ether, and desiccated with fused caustic soda. The residue left after the ether was driven off was distilled.

The results obtained in tests run at different temperatures are listed in Table 1.

TABLE 1

Test temperature	Quantity of 2-butyne-1,4-diol, grams	Catalyzate		
		B.p.	Quantity, g	n_D^{20}
350°	10	130-133°	0.3	1.4893
400	10	130-133	0.75	1.4970
450	10	130-133	0.5	1.4979
500	10	130-133	0.47	1.4923

Redistillation of the combined pyrrole fractions yielded pure pyrrole with a b.p. of 130-131.5° (760 mm).

3. Joint dehydration of 2-butyne-1,4-diol and hydrogen sulfide. 10 g of 2-butyne-1,4-diol was passed over alumina at 350° in a current of hydrogen sulfide at the rate of 6-8 drops per minute. The catalyzate was washed with caustic soda and extracted with ether. After the ether had been driven off from the desiccated ethereal extract, the substance was distilled at 83-85° (0.3 g); it exhibited a positive indophenine reaction.

The product of the reaction of 10 g of 2-butyne-1,4-diol with hydrogen sulfide over alumina at 400° yielded 0.5 g of a substance with a b.p. of 84° (758 mm), which exhibits an indophenine reaction and is found to be thiophene.

4. Joint dehydration of cis-2-butene-1,4-diol. a) Cis-2-butene-1,4-diol. 20 g of 2-butyne-1,4-diol in 60 ml of absolute alcohol was hydrogenated in the cold with 3 g of Raney nickel. One equivalent of hydrogen (5612 ml at 21°) was absorbed in 8 hours; this yielded 17 g (80.3% of the theoretical) of cis-2-butene-1,4-diol:

B.p. 115-116° (3 mm); n_D^{20} 1.4734; d_4^{20} 1.0363; MR_D 23.87.
$C_4H_8O_2$. Computed: MR_D 23.50.

Literature data for cis-2-butene-1,4-diol: Johnson [7] - B.p. 134-135° (15 mm); n_D^{25} 1.4716; Prevost and Valette [8] - B.p. 131-132° (14 mm); n_D^{15} 1.479; d_4^{15} 1.082.

b) Catalytic dehydration of cis-2-butene-1,4-diol. 10 g of cis-2-butene-1,4-diol was heated with 2 g of the aluminosilicate. A colorless liquid began to distil over at 160-170°. The distillate was saturated with sodium sulfate, and the top layer (4 g) was separated and desiccated with anhydrous sodium sulfate.

25 g of cis-2-butene-1,4-diol yielded a total of 10 g of the desiccated substance. The following fractions were collected during distillation into a column with 25 theoretical trays:

1 - B.p. 63 - 65.5° (768 mm) - 0.7 g
2 - B.p. 65.5° (768 mm) - 2 g
3 - B.p. 65.5-67° (768 mm) - 0.6 g
4 - B.p. 67 - 100° (768 mm) - 1 g
5 - B.p. 100- 102° (768 mm) - 1.3 g.

The dihydrofuran recovered after repeated distillation (over metallic sodium) of Fractions 1, 2, and 3 (33% yield, based on the resulting dehydration product) possessed the following constants:

B.p. 65.5-66° (767 mm); d_4^{20} 0.9223; n_D^{20} 1.4249; MR_D 19.43.
C_4H_6O. Computed: MR_D 19.64.

Literature data for dihydrofuran: Pariselle [9] - B.p. 67-69° (760 mm); n_D^{15} 1.4400; d_4^{15} 0.9450; Yu.K.Yuryev [10] - B.p. 65.5-67.5° (745 mm); n_D^{20} 1.4310; d_4^{20} 0.9436.*

Synthesis of 3,4-dibromotetrahydrofuran, (3,4-dibromofuranidine). A chilled solution of 0.6 g of bromine in 3 ml of carbon tetrachloride was added, with strong chilling, to a solution of 0.8 g of dihydroguran in 3 ml of carbon tetrachloride, and the reaction mass was set aside to stand overnight. The 3,4-dibromofuranidine had the following constants after the carbon tetrachloride had been driven off and it had been double distilled:

B.p. 90.5-91.5° (19 mm); n_D^{20} 1.5490; d_4^{20} 2.0414.

Literature data for 3,4-dibromofuranidine: Henninger [11] - b.p. 95° (20 mm); m.p. 12°. Pariselle [9] - b.p. 97-99° (24 mm); m.p. 10-11°.

The crotonaldehyde recovered after repeated distillation of Fractions 4 and 5 (23% yield) had the following constants:

* The constants of the dihydrofuran produced in the present research differ somewhat from those cited in the papers by Pariselle and by Yu. K. Yuriev, who synthesized dihydrofuran by using caustic soda to detach hydrogen bromide from β bromofuranidine.

B.p. 100-102° (758 mm); n_D^{20} 1.4352; d_4^{20} 0.854; MR_D 22.30.
C_4H_6O. Computed: MR_D 22.42.

3.335 mg substance; 8.385 mg CO_2; 2.530 mg H_2O.
5.380 mg substance: 13.540 mg CO_2; 4.082 mg H_2O.
Found %: C 68.57; 68.54; H 8.49, 8.49.
C_4H_6O. Computed %: C 68.56; H 8.62.

The semicarbazone fused at 186-187° after being recrystallized from ethyl alcohol. The semicarbazone of crotonaldehyde has a m.p. of 187°. A mixed test sample exhibited no depression during fusion, melting at 187°.

Literature data for crotonaldehyde: Enklaar [12] - b.p. 102.2-102.5° (762 mm); $n_D^{20.5}$ 1.4362; $d_4^{20.5}$ 0.8477; Auwers and Heimke [14] - m.p. of the semicarbazone of crotonaldehyde: 198-199°; Auwers and Eisenlohr [13] - n_D^{23} 1.4348; $d_4^{17.3}$ 0.8557.

SUMMARY

1. The catalytic dehydration of 2-butyne-1,4-diol over alumina results in the formation of furan, but the principal reaction is the decomposition of the diol and the evolution of acetylene.

2. The catalytic dehydration of 2-butyne-1,4-diol with ammonia and with hydrogen sulfide results in the formation of pyrrole and thiophene, respectively.

3. The catalytic dehydration of cis-2-butene-1,4-diol runs along two lines, the reaction products being dihydrofuran and crotonaldehyde.

LITERATURE CITED

[1] Yu. K.Yuryev. The Transformation of Oxygen-Containing Heterocyclic Systems into Rings with Different Heterocyclic Atoms and into Hydrocarbons. Monograph, Sci. Papers Moscow State Univ., 79, 122 (1945); Yu.K.Yuryev and Medovshchikov, J.Gen. Chem. 9, 628 (1939).

[2] A.Valette, Comptes rendu., 223, 907 (1946).

[3] L.Ilosvay, Ber., 32, 2697 (1899).

[4] R.Wiegman, Z.phys.Chem., 2, 237 (1888).

[5] T. Peterson and D.Thomson, J. Chem. Soc., 93, 371 (1908).

[6] F. Straus and L.Kollek, Ber., 59, 1664 (1926).

[7] A.Johnson, J.Chem.Soc., 1946, 1009.

[8] Ch.Prevost and A.Valette, Comptes rendu., 222, 326 (1946).

[9] H. Pariselle, Comptes rendu., 148, 849 (1909).

[10] Yu.K.Yuryev, Sci.Papers Moscow State University, 79, 98 (1945).

[11] K.Henninger, Ann. Chim., (6) 7, 219 (1886).

[12] G.Enklaar, Ber., 49, 211 (1916).

[13] K.Auwers and F.Eisenlohr, J. prak. Chem., (2) 82, 116 (1910).

[14] K.Auwers and P.Heimke, Lieb. Ann., 458, 254 (1927).

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